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HAZARDOUS WASTE  
JULY 1989

ALSO

X-Met 820

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# X-MET 880

PORTABLE, WIDE RANGE  
XRF-ANALYZER



## THE X-MET 880

- is the newest model in the X-MET line of XRF analyzers
- performs rapid non-destructive analyses of elements
- is designed for field and industrial use

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# Simultaneous analysis of six elements from liquid, powder and solid samples

The X-MET 880 can be equipped with one to six probes (with a Fe-, Cd-, Cm- or Am-source). Therefore the instrument is capable of analysing all the elements from aluminium to uranium. There can be 32 different programs

(calibration models) at a time, each capable of analysing up to six different elements simultaneously. Reprogramming to a different application is possible. The X-MET 880 gives analyses from liquid, powder or solid samples.



## X-MET 880

- Expanded 400 spectra reference library
- New dual source surface probe
- Automatic multiprobe switch box
- Storage for 32 multielemental programs
- Improved built-in keyboard and LCD display
- Surface probes for in situ analysis
- Modular design for customized configuration to meet specific analytical needs
- Built-in battery for 10 hours of field use
- Interface to IBM PC or compatible.

Elements:

Measurement method: Energy dispersive XRF

Measurement capacity: Simultaneous analysis of six freely selectable elements with 32 computing programs (calibration models)

Waterproof class: IP55

Temperature: -25°C to +60°C

Voltage: 115/230 V  $\pm$  20 % 49 to 61 Hz

Power requirement: 20 W

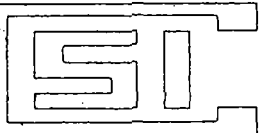
Weight: 8.5 kg (complete with surface probe SAPS)

Also benchtop and on-line models available.  
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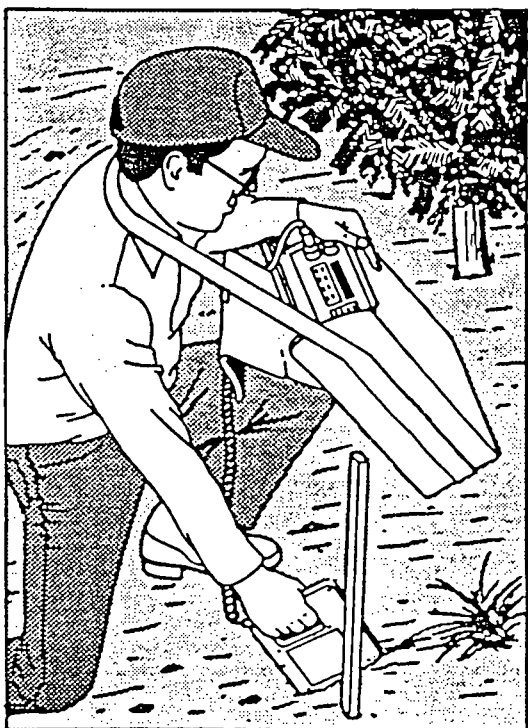
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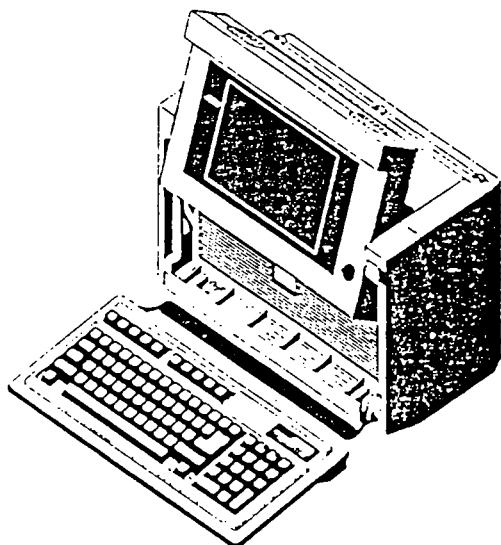
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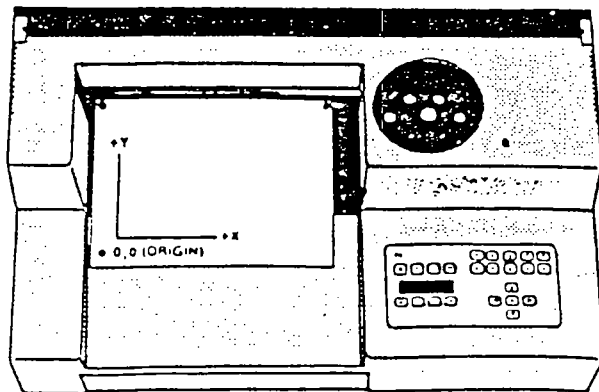
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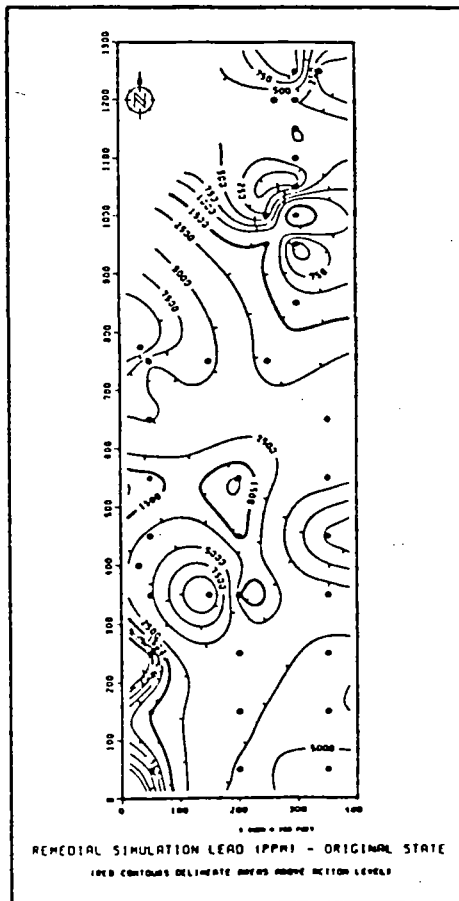
### Data Transfer & Processing



### Plotting



EMSL-LV Project Manager: L.A. Eccles



### Final Product



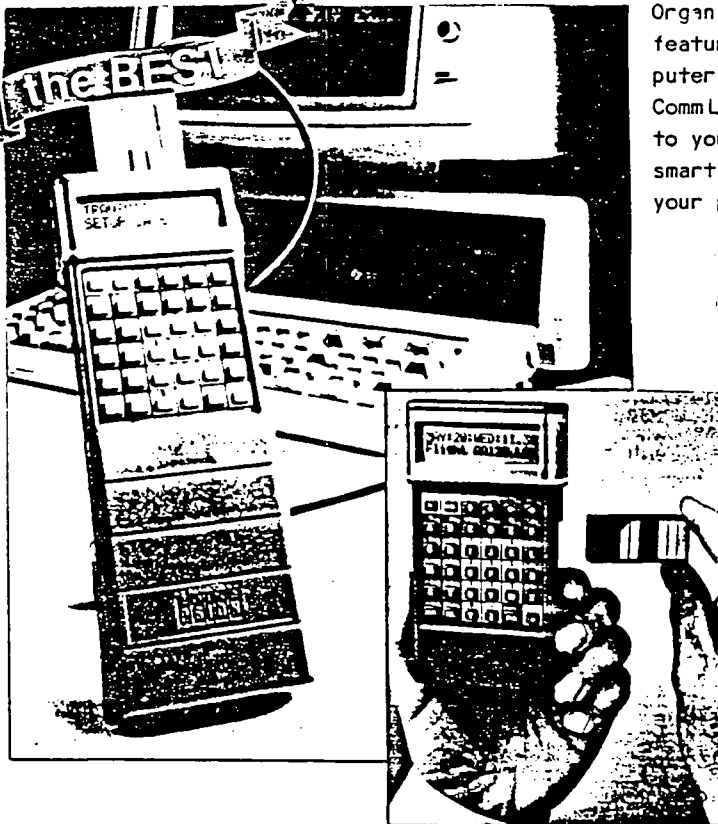
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Solid state EPROM memory units come in 16K to 128K capacity for virtually unlimited memory.

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STANDARD features of this sleek, precision-crafted instrument: 50 function scientific calculator, appointment scheduler, diary, alarm, clock/calendar and more.





# Analysis of Hazardous Material

## WITH PORTABLE X-RAY ANALYZER

### 1. INTRODUCTION

The implementation of the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation and Liability Act (Superfund) has increased the need to measure the chemical characteristics of wastes. The nature of the problem requires the measurements to be rapid and inexpensive yet with uncompromised accuracy and precision. Moreover, most of the critical testing has to be done in the field rather than in laboratory conditions if the program of

environmental monitoring is to be cost effective and timely.

The Model 840, a battery operated Portable X-ray Analyzer, with its rugged and splashproof construction, is very well suited for such a task. It provides rapid, field screening analysis of hazardous waste samples — be they contaminated soil or liquid — for "heavy metals" (and non-metals), in a matter of one to four minutes per sample. The contaminating elements usually being determined include such recognized toxic elements as:

ARSENIC	CADMIUM	LEAD	SELENIUM
BARIUM	CHLORINE	MERCURY	SILVER
BROMINE	CHROMIUM	NICKEL	THALLIUM
COPPER		ZINC	

### TYPICAL MATERIALS ANALYZED ARE:

- Samples of soil collected at the chemical waste dump site
- Liquids such as waste oil
- Vegetation
- Swabs and tissues from wipe tests
- PCBs in transformer oil

### 2. EXAMPLES OF APPLICATION

#### ANALYSIS OF HAZARDOUS WASTE CONTAMINATED SOIL

##### MEASUREMENT CONDITIONS

- |                       |  |
|-----------------------|--|
| • Material analyzed:  | powdered soil                                    |
| • Elements measured:  | As, Cu, Zn, Pb                                   |
| • Probe:              | Sample Probe,<br>Type HEPS (Xe/CO <sub>2</sub> ) |
| • Radioactive source: | 100mCi Cm-244                                    |
| • Measurement time:   | 200 sec/sample                                   |

##### COMMENTARY

The 840 system was calibrated to measure mg/kg of arsenic, copper, zinc and lead in soil contaminated with hazardous waste. A set of 18 analyzed samples of contaminated, pow-

dered soil was used for calibration. The calibration samples were used "as received"\* and were assumed to be homogeneous and representative of the sampled material. An aliquot

\* Samples and referee analyses courtesy of Tetra Tech, Inc.



# FIG 1 to 5

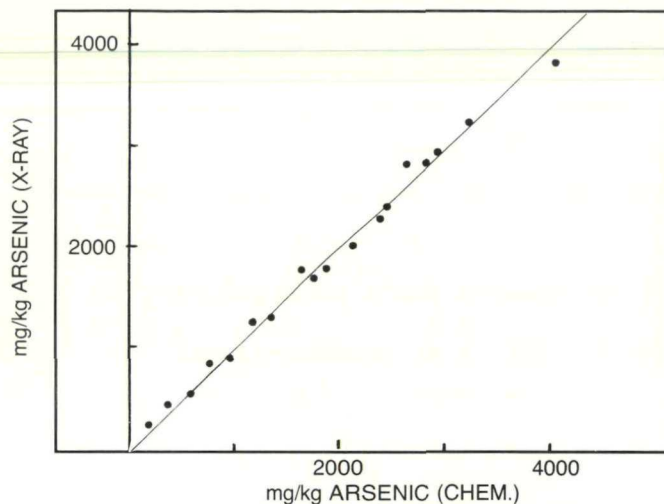


Fig. 1 ARSENIC IN CONTAMINATED SOIL

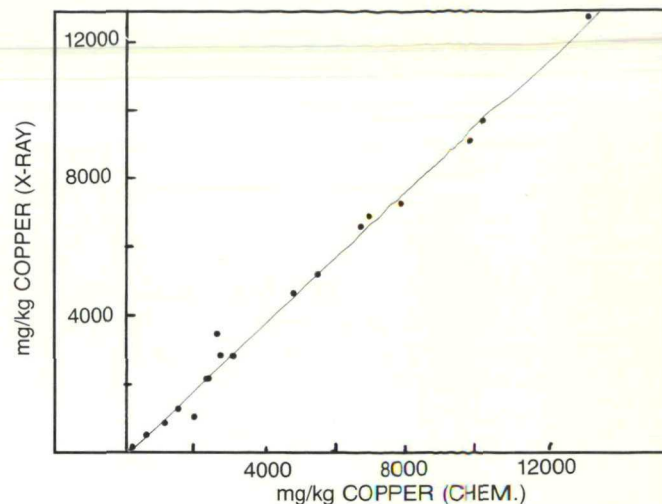


Fig. 2 COPPER IN CONTAMINATED SOIL

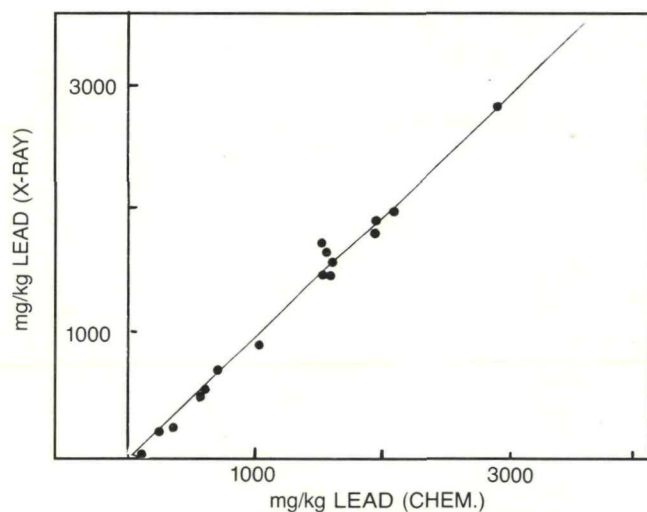


Fig. 3 LEAD IN CONTAMINATED SOIL

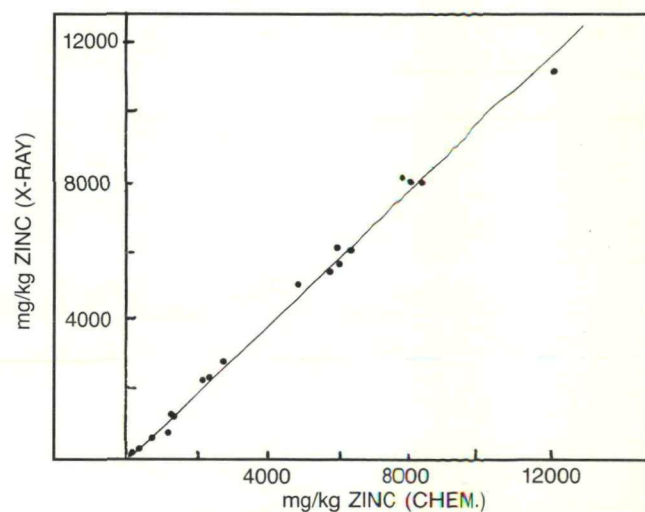


Fig. 4 ZINC IN CONTAMINATED SOIL

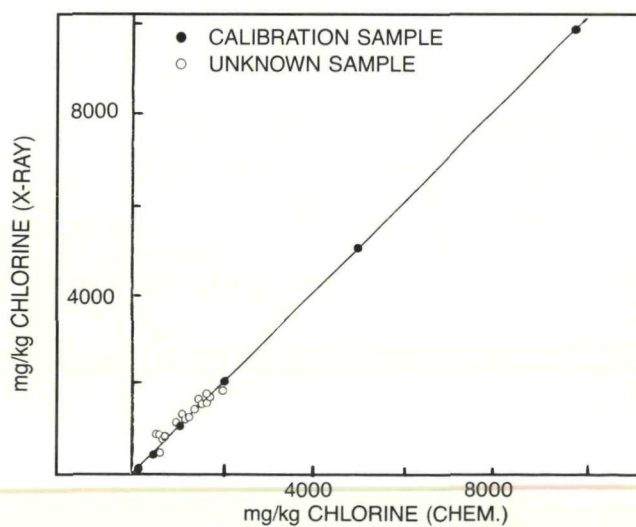


Fig. 5 CHLORINE IN WASTE OIL

of about 5 gm of each sample was transferred into a plastic cup with a 6 micron thick polypropylene X-ray window, and then placed in the probe for measurement.

Any sample of natural soil always contains some iron, silicon, aluminum, calcium, strontium, rubidium — the elements characteristic of the Earth's crust. Of these, iron and rubidium are likely to interfere with quantitative determination of the elements measured. In order to correct for this interference the instrument was set to record for each sample the X-ray inten-

sities of the interfering elements in addition to those of the elements of interest.

Element intensity and concentration data for each calibration sample were employed to develop optimum calibration for each element of interest using a multiple linear regression algorithm, which is an integral part of the 840 software.

Figures 1 to 4 show typical calibration plots, as obtained for As, Cu, Zn, and Pb. Table 1 contains the results obtained with the calibrated 840, as compared with the referee analysis. Table 2 summarizes the error data.

## ANALYSIS OF USED OIL SAMPLES FOR TOTAL CHLORINE

### BACKGROUND INFORMATION

It is estimated that about 500 million gallons of used oil are burned each year in some 30,000 boilers and industrial furnaces in the U.S.A. Since used oil is often mixed with spent chlorinated solvents, a real danger exists that boilers may emit hazardous levels of solvents to ambient air, creating a cancer risk to humans.

In November 1985, EPA published the rules on use and management of used oil. The final regulation bans sale of used oil for fuel to

nonindustrial users if the total halogen content of the oil exceeds the level of 1000 mg/kg. As a consequence of this regulation, the regulated community and the enforcement authorities will have to determine total halogens in used oils and fuels. Ideally, such determinations would be carried out in the field.

Because a total halogen determination cannot be easily made either in the field or laboratory, EPA has agreed to interpret "total halogen" as total chlorine.

### MEASUREMENT CONDITIONS

- |                       |                               |
|-----------------------|-------------------------------|
| • Material analyzed:  | used crankcase and fuel oil   |
| • Elements measured:  | chlorine                      |
| • Probe:              | Light Element Probe, Type LEP |
| • Radioactive source: | 20mCi Fe-55                   |
| • Measurement time:   | 200 sec/sample                |

## COMMENTARY

A set of 6 analyzed samples of virgin oil\* (samples 1A to 6A in Table 3), covering the range of 0 to 10000 mg/kg chlorine, were used to calibrate the 840 system to measure chlorine in samples of virgin and waste crankcase and fuel oil.

Each sample was shaken in its bottle and then three 5 ml aliquots were withdrawn from each bottle for measurements. Each aliquot was measured for 200 seconds in a plastic cup with a 6 micron thick polypropylene X-ray window. Calibration was completed by fitting a calibration equation to the chlorine x-ray intensity vs concentration data, using the 840 resident software.

Table 3 lists the results obtained on samples of virgin (A-series) and waste (F-series) crankcase oil. Table 4 lists all pertinent calibration and error data.

The same system can measure total chlorine in other liquids such as transformer oil (contaminated with Aroclors) or wood preservative liquors (containing pentachlorophenol or "PENTA"). Since the 840 can simultaneously store up to eight (8) different calibrations, the instrument can be prepared to measure chlorine in any kind of medium encountered in practice.

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\* Samples and referee analyses courtesy of Research Triangle Institute.



# TABLE 1. RESULTS OF ANALYSIS — CONTAMINATED SOIL

SAMPLE	CONCENTRATION OF ELEMENT IN mg/kg							
	ARSENIC		COPPER		LEAD		ZINC	
	GIVEN	MEASURED <sup>a</sup>	GIVEN	MEASURED	GIVEN	MEASURED	GIVEN	MEASURED
1	1680	1804 ± 32 <sup>b</sup>	2900	2878 ± 28	735	740 ± 38	2270	2314 ± 32
2	1800	1736 ± 36	2450	3497 ± 34	1580	1769 ± 43	5780	6139 ± 45
3	1200	1283 ± 29	2580	2826 ± 28	643	595 ± 37	2690	2762 ± 33
4	990	954 ± 23	1080	1025 ± 18	257	225 ± 33	1070	719 ± 20
5	600	593 ± 19	449	502 ± 14	60	0 ± 32	254	292 ± 15
6	780	895 ± 24	2210	2176 ± 24	389	265 ± 34	1250	1243 ± 26
7	1380	1366 ± 27	1330	1252 ± 20	607	515 ± 36	1160	1250 ± 23
8	390	488 ± 19	925	892 ± 16	133	40 ± 32	521	517 ± 18
9	2640	2854 ± 45	6730	6989 ± 45	1600	1696 ± 44	6150	6055 ± 52
10	2460	2470 ± 44	9580	9216 ± 53	1610	1529 ± 43	7880	8033 ± 60
11	2820	2884 ± 49	9970	9854 ± 54	2090	2047 ± 46	8180	8035 ± 61
12	2940	2980 ± 45	5240	5232 ± 40	1970	1886 ± 45	5600	5423 ± 47
13	4080	3880 ± 61	12800	12980 ± 66	2910	2912 ± 51	11800	11240 ± 74
14	2170	2130 ± 42	6480	6642 ± 46	1630	1620 ± 43	7630	8193 ± 56
15	3240	3290 ± 48	7600	7329 ± 46	1930	1960 ± 46	5850	5644 ± 51
16	2400	2319 ± 39	4570	4669 ± 37	1580	1523 ± 42	4700	5091 ± 44
17	1930	1817 ± 31	2130	2159 ± 25	1060	967 ± 39	2070	2272 ± 30
18	200	294 ± 18	34	53 ± 11	16	0 ± 31	77	104 ± 12
20 <sup>c</sup>	2820	2819 ± 49	11000	11000 ± 58	2160	1926 ± 45	8760	8226 ± 63
21	1800	1617 ± 30	2580	2529 ± 27	815	732 ± 37	2460	2601 ± 32
22	200	311 ± 18	28.5	33 ± 11	17	0 ± 31	64	107 ± 12
23	7.5	140 ± 16	12	62 ± 10	7	0 ± 30	183	223 ± 12
24	23	293 ± 21	18	61 ± 12	6.5	0 ± 31	420	527 ± 15
25	1330	1229 ± 26	1280	1308 ± 20	465	417 ± 35	1050	1035 ± 23

- NOTES:
- a) All measurements 200 sec each
  - b) One standard deviation of counting statistics
  - c) Samples 20-25 are unknowns and were not included in the calibration of the instrument. Concentration data for these samples were revealed only after the 840 measurements were reported to the customer.

**TABLE 2. ASSESSMENT OF ERRORS**

	ARSENIC	COPPER	LEAD	ZINC
CONCENTRATION RANGE MG/KG	0-4000	0-13000	0-3000	0-12000
CORRELATION COEFFICIENT	.996	.997	.991	.995
RMS ("TOTAL") ERROR <sup>a</sup>	± 110	± 280	± 115	± 360
INSTRUMENTAL REPEATABILITY <sup>b</sup>	± 31	± 21	± 35	± 23
ERROR DUE TO HETEROGENEITY OF SAMPLE <sup>c</sup>	± 15	± 16	± 45	± 25
DETECTION LIMIT: INTERFERENCE FREE <sup>d</sup>	55	30	90	36
WITH INTERFERENCE <sup>e</sup>	150	70	120	80

Units are [mg /kg]. All errors quoted for 200 sec.

**NOTES**

- a) As spread of the experimental data around the fitted calibration curve.
- b) As one std. deviation of a series of at least ten consecutive measurements taken on the same, undisturbed sample.
- c) As one std. deviation of a series of at least ten measurements taken on various (or repoured) aliquots of the same sample corrected for counting statistics error.
- d) As 3 std. deviations of counting statistics obtained on "blank" sample (with elemental concentrations at zero level).
- e) As above but on sample with lowest possible concentration of given element and high concentration of the other elements present.

# TABLE 3. TOTAL CHLORINE IN OIL

Sample	TOTAL CHLORINE IN mg/kg:				Remarks
	Referee Analysis	As Measured With The 840 In Three Aliquots Of The Same Sample			
1A	156	81	191	230	Calibration Samples
2A	500	455	424	400	
3A	1140	1070	1046	1046	
4A	2123	2110	2113	2176	
5A	5075	5081	5252	5080	
6A	9994	9926	9935	9928	
A1	717	771	788	704	Virgin Crankcase Oil
A2	1758	1667	1728	1732	
A3	1197	1339	1069	1154	
A4	1156	1066	1026	1037	
A5	675	468	519	568	
A6	1759	1673	1631	1736	
A7	580	912	894	935	
A8	1197	1346	1375	1536	
A9	1660	1662	1675	1719	
A10	1071	1179	1250	1271	
A11	645	889	859	913	
A12	1559	1618	1672	1640	
A13	1610	1519	1556	1461	
A14	1032	1080	1120	1069	
A15	791	886	938	917	
D1	1193	1012	1051	1103	#2 Fuel Oil
E1	1101	1022	910	883	#6 Fuel Oil
F1	1321	1244	1283	1301	Waste Crankcase Oil
F2	1817	1718	1727	1677	
F3	1226	1226	1250	1231	
F4	2076	1877	1858	1860	
F5	1476	1472	1411	1485	
F6	1726	1603	1638	1674	



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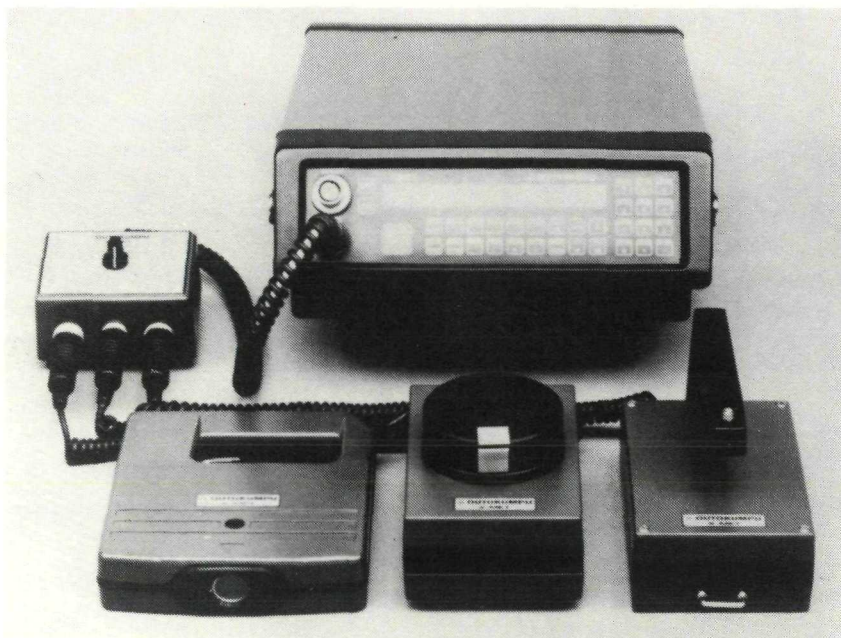




**TABLE 4. ASSESSMENT OF ERRORS  
— TOTAL CHLORINE IN OIL**

Parameter	Correlation Coefficient	Instrumental Repeatability <sup>a</sup>	RMS ("Total") Error <sup>b</sup>	Detection Limit <sup>c</sup>
Parameter Value	.9999	± 30 to ± 60 mg/kg <sup>d</sup>	± 55 mg/kg	± 100 mg/kg

- Notes:
- a) As one standard deviation of a series of at least ten consecutive measurements taken on the same, undisturbed aliquot.
  - b) As spread of the experimental data around the fitted calibration curve.
  - c) As 3 std. deviations of counting statistics obtained on "blank" sample (with element concentration at zero level).
  - d) Smaller value at 0 mg/kg chlorine, larger value at 10,000 mg/kg chlorine.



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# A New Calibration Technique For X-Ray Analyzers Used In Hazardous Waste Screening

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## ABSTRACT

The rapid increase of interest in the use of X-ray fluorescence for on-site elemental analysis of solid hazardous waste is justified by the many advantages of the technique for this application; for example, multi-element capability over wide concentration ranges (100 mg/kg to 100%), speed of measurement, potential for little or no sample preparation, and availability of low-cost field-portable instrumentation.

One important difficulty has been in the area of calibration samples and methods. Calibration samples are required (1) to cover the many elements measurable over wide concentration ranges, (2) to enable possible interferences to be corrected for and (3) to physically match the analyzed material, particularly in particle size.

The best available reference materials (finely powdered geochemical and mineral standards) do not contain nearly enough elements in appropriate concentrations, do not match the particle size of the material to be analyzed and are too few in number. The use of real samples analyzed by a referee method is expensive, time-consuming and imposes the errors of the referee method on the X-ray analyses.

This paper describes the preparation and use of calibration samples made by spiking uncontaminated soil with the elements of interest. These samples can be made to cover all the necessary parameters and are independent of any referee method. They can physically match the material to be analyzed so well that good results are obtained on coarse material without further sample preparation.

Measurement results using a commercially available portable XRF analyzer are given for the determination of Cu, Zn, As and Pb in contaminated soils. The results agree very well with independent referee analyses of the same soils.

## INTRODUCTION

While it may seem obvious that in order to map the distribution of toxic chemicals at a hazardous waste site one has to measure the chemical characteristics of the site, the answer to "how to accomplish it in a reliable and cost-effective manner" is not trivial.

Three categories of analytical requirements are recognized by the U.S. EPA<sup>1</sup>. The highest level, Level One, consists of the most accurate and precise analytical methods used for measurement. They are also the most expensive, labor-intensive and time-consuming. Such analyses are always performed in laboratory conditions and are used to provide data for litigation or enforcement procedures under the Contract Laboratory program. Second Level analysis is used to assess average pollutant exposures to humans and animals and does not require the highest degrees of accuracy and precision. Third Level analysis—called screening—provides data for insitu deline-

ation of sites or hot spots and for selecting samples to be sent for First and Second Level analyses.

In order to be effective, screening analysis has to be fast, simple and operable in the field. However, it still has to provide the necessary accuracy and precision.

The criteria mentioned above make x-ray fluorescence (XRF) the technique of choice for on-site screening analysis of hazardous waste for "Heavy Metals." XRF has many advantages over other elemental analysis techniques such as atomic absorption (AA) and inductively coupled plasma (ICP) techniques, including multi-element capability over wide concentration ranges, little or no sample preparation, portability, nondestructive character and ability to perform measurements in the field.

## XRF BASICS

X-ray fluorescence spectrometry is a well-established, comparative, analytical technique which utilizes the Physical principles of the interaction of x-rays or gamma rays with matter. When a sample of material is exposed to an external beam of low energy (1 to approximately 100 keV) x-rays or gamma rays, the main result is excitation of atoms in the sample. The excited state of the atom is achieved when the incident quantum of radiation from the external source has a high enough energy to remove an electron from the inner energy shell of the atom. The vacancy created is filled almost instantly by an electron from a higher energy shell, the excess energy being released in the form of an x-ray photon. The energy of this photon is unique for any given element and therefore can be used to identify the presence of that element in the sample. The number of photons of a given energy is—in turn—representative of the number of atoms of that element in the sample, or—in "macroworld" terminology—the element concentration of the sample.

The apparently simple process described above is in reality more complex due to interferences inherent in the technique. These must be addressed for accurate analysis to be feasible, and much literature exists on the topic<sup>2,3</sup>.

## PORTABLE X-RAY ANALYZER FOR ANALYSIS OF HAZARDOUS WASTE

Practical XRF analyzers fall into two main categories depending on whether they employ wavelength dispersive (WDXRF) or energy dispersive (EDXRF) spectrometry to sort the characteristic x-rays from the sample. While WDXRF spectrometers have the advantage of high spectral resolution, they are usually bulky and expensive. Also they are less efficient in their usage of x-rays than their EDXRF counterparts and thus require high power x-ray tube

sources. EDXRF spectrometers, being more efficient, can operate with small radioactive sources instead of x-ray tubes and thus can more readily be made into portable, field operated instruments.

A portable x-ray analyzer configured for hazardous waste analysis consists of a probe and electronic unit. The probe contains an x-ray source, a detector to measure x-ray intensity and resolve the x-ray spectrum, and a sample chamber which can accommodate samples in a reproducible manner. The electronic unit accepts the signal from the probe, performs all the necessary data processing and displays the result. It also contains power supplies and interfaces for communication with the operator and peripheral devices.

The preferred source for portable instruments is a sealed radioisotope capsule that emits x-rays or low energy gamma rays. Such sources are rugged, compact, lightweight and free from drift problems. Since their output is about six orders of magnitude less than that of an x-ray tube, the characteristic x-rays from the sample must be resolved and measured with high geometrical efficiency.

Three types of detector that can do this are employed: scintillation counters, proportional counters and solid state (silicon) detectors. The scintillation counter has the poorest x-ray resolution and requires balanced filters to help discriminate the characteristic x-rays. Two filters are needed per element, with a minimum of  $n + 1$  filters for  $n$  neighboring elements. This creates considerable mechanical complexity in an automatic filter changer for approximately 10 elements. Also, since the filters have to be changed to go from one element to the next, multi-element measurements are sequential which considerably adds to the analysis time. However, a successful portable analyzer employing this principle is in use<sup>4</sup>.

The solidstate detector can completely resolve K x-rays from neighboring elements but requires cryogenic cooling while in operation. This is bulky and expensive whether liquid nitrogen or a thermoelectric method is employed for cooling. Completely portable analyzers have not yet been developed, but transportable units with hand held probes are in use<sup>5</sup>.

Proportional counters have a resolution intermediate between scintillation counters and silicon detectors. Cryogenic cooling is not required. Until recently, the resolution of proportional counters was not good enough to avoid the need for balanced filters. However, new developments in proportional counter technology have yielded detectors with significantly improved resolution (10-12% for the FeK line)<sup>6</sup>. This detector, coupled with a microprocessor for spectral processing, has resulted in the availability of a hand-portable x-ray fluorescence analyzer, capable of simultaneous multi-element analysis that does not require either balanced filters or cryogenic cooling<sup>7</sup>.

## CALIBRATION OF XRF ANALYZERS

As mentioned earlier, x-ray fluorescence spectrometry is a comparative analytical technique and as such requires a number of well-characterized samples for calibration. The number of calibration samples is determined by the number of elements to be measured, the variability (range) of each analyte and the overall complexity of the sample matrix. Therefore, the number of samples required for calibration may vary from just a few to approximately 30 or more.

### *Matrix effects due to chemical composition*

It is obvious that any sample contains more than just the element of immediate interest to the analyst. The other elements present in a sample can significantly affect the results of analysis.

Suppose the concentration of iron in sand (i.e., silica) is to be measured. The x-ray intensity of iron will be reduced by that amount absorbed in the sand matrix and also in the iron bearing component. If the sand contains some calcium carbonate, the iron x-rays likely will be absorbed even more because calcium absorbs x-rays more than the silica it replaced. This is called the matrix absorption effect, and calcium plays the role of absorber in relation to the iron analyte. However, should copper be substituted for calcium,

then the measured intensity of iron x-rays could be increased since the characteristic K x-rays of copper can excite additional atoms of iron. This effect is called matrix enhancement, and copper is an enhancer for the iron analyte.

In both cases, the measured intensity of the analyte alone would provide a false representation of its concentration in the sample. To prevent this, mathematical corrections can be applied to the intensity of the analyte before it is converted to percent concentration.

There are several well established theoretical models for mathematical corrections of matrix effects<sup>2,3</sup>, each with its advantages and disadvantages. All models, however, are based—either directly or indirectly—on the assumption that the degree of interference of the matrix element with the analyte intensity is, at least to a first order approximation, proportional to the concentration of interfering element in the sample. This procedure allows the correction model to be a relatively simple set of calibration equations with constant coefficients.

The coefficients can be calculated by applying a multivariable, linear least squares algorithm to the intensity data obtained from a properly chosen set of calibration samples. Corrections of this type can be easily performed by the software package supplied with the XMET portable analyzer.

### *Matrix effects due to particle size*

Another source of error in XRF analysis of particulate samples is the variability of particle size of the sample material.

Samples of soil are naturally heterogeneous in many ways. Not only can particulates of soil vary over a wide range of sizes and shapes, but the analyte itself can be distributed in the sample in a very nonuniform fashion. Quite often the effect of Particle size is greater than that of chemical composition although both are different manifestations of the basic phenomenon of absorption of x-rays in the sample medium. An excellent discussion of this subject is presented by Berry, et. al.<sup>8</sup>.

Particle size effects are totally removed only by reducing the grain size of the sample to zero. This condition can be achieved by fusion or dissolution of the sample, but only in the laboratory, and then all the benefits of on-the-spot XRF analysis are forfeited.

Corrections for particle size effects also can be made by using theoretical models. However, an empirical approach in which both the unknown and the calibration samples are prepared in the same way is much more effective. This assures that any interferences due to particle size are the same for measured and calibration samples.

### *Criteria for calibration samples*

The facts discussed so far allow a listing of essential features of an ideal set of calibration samples as follows:

- The chemical composition of the sample matrix should be as close as possible to the composition of that of the unknown.
- Calibration samples must contain all elements of interest at concentrations matching the expected concentration ranges in the unknowns.
- The number of calibration samples must be sufficient to allow for reliable correction of matrix effects. For example, approximately 20 samples are needed to calibrate the analyzer for measurement of four different elements.
- The physical characteristics of calibration samples (particle size, moisture content, etc.) should resemble those of the unknown.
- It must be possible to prepare calibration samples in quantity and inexpensively.

Unfortunately, suitable materials have not been hitherto available for calibration of x-ray analyzers for hazardous waste analysis. Finely powdered geochemical and mineral reference materials, such as those provided in limited quantities by NBS or CANMET, have been considered. However, these standards do not meet any of the requirements listed above, and therefore cannot be used for routine calibration of portable x-ray equipment.

To circumvent the problem, it is possible to either calibrate the



instrument with real samples analyzed by a referee method or to develop synthetic reference samples. While the first alternative is theoretically preferable, it is very expensive, is time-consuming and carries the errors of the referee analysis. Also, it often would be impossible to provide adequate concentration coverage without performing referee analysis on a large number of samples typical of the site to be mapped. This procedure, of course, defeats the objectives of rapid field screening.

It is clear that the successful development of a suitable calibration technique for hazardous waste screening with portable x-ray analyzers would benefit all interested parties. Such an effort, based on preparation of synthetic reference materials, is reported in this paper.

#### PREPARATION OF SYNTHETIC CALIBRATION SAMPLES

Although to the authors' knowledge there is no officially recommended procedure for sampling and analysis of contaminated soil, the generally accepted practice one should use at this time is as follows:

- Collect a sample of 100 to 200 g. of soil (alternatively 100 to 200 ml. of soil)
- Dry the sample at 105° C.
- Remove foreign objects such as twigs, feathers, grass, bugs and pebbles
- Break up agglomerates and lumps (but do not grind)
- Sieve the material through a 10 mesh sieve (2mm opening size) and collect the undersize fraction

At this point, an aliquot usually would be withdrawn for analysis by AA or ICp. However, if an x-ray analysis is planned, the last step would be preceded by grinding the sample to 200 mesh and then an aliquot would be submitted for analysis on the x-ray spectrometer.

The first four steps have to be followed regardless of the analyti-

cal method used. Therefore, the authors decided to develop calibration standards which would not require the user to grind his assay sample to 200 mesh, thus avoiding a very time-consuming step in the procedure.

#### Preparation of Calibration Samples

In order to obtain material for making calibration samples approximately 8 kg. of soil were collected from an area known to be free of pollutants. After receiving the sample in the laboratory, the soil was oven-dried at 105° C to constant weight and then allowed to equilibrate to ambient humidity and temperature. The initial moisture content of the soil 11.5%. Subsequent uptake of moisture at room temperature was 2.0%.

The soil was then run through an 8 mesh sieve to yield about 5 kg. of material finer than 2.4 mm in diameter. An aliquot of this material was analyzed on a high resolution x-ray spectrometer. As expected, the soil contained the elements typical of the earth's crust, viz, Al, Si, K, Ca, Fe and minor amounts of Sr, Rb, Zr and Y. Traces of Cu and Zn also were noticed. The soil appeared to be of a sandy nature.

Sixteen 100g. aliquot of this soil were weighed into clean containers. Each aliquot was then spiked with appropriate amounts of potentially hazardous elements.

Four elements were selected for the spiking experiment; zinc, copper, arsenic and lead. These four elements are good examples of toxic soil contaminants and also represent the main types of x-ray interferences. The Cu/Zn and Pb/As pairs exhibit spectral overlap, whereas Cu and Zn absorb Pb and As x-rays which in turn enhance Cu and Zn x-rays.

Sixteen mixtures containing these elements in non-correlated concentrations were prepared gravimetrically from analytical grade components and subsequently were used to spike each 100g. sample of soil. Final values of concentrations of spiking elements in each sample are listed in Table 1. The absolute error of each element concentration in the samples is estimated at  $\pm 2$  mg/kg. After

Table 1  
Concentrations of Spiking Elements in Calibration Samples

CALIBRATION SAMPLE NUMBER	mg/kg OF ELEMENT ADDED TO EACH SAMPLE			
	COPPER	ZINC	ARSENIC	LEAD
1 B	4790	4790	6790	980
2 B	0	0	11340	0
3 B	0	0	0	4980
4 B	9530	95	9330	95
5 B	8160	240	7740	240
6 B	6300	482	5590	484
7 B	3810	1900	11070	4760
8 B	2950	983	4530	1474
9 B	982	2970	3390	1990
10 B	1960	3910	2250	2930
11 B	490	6360	1140	2440
12 B	243	8270	565	3405
13 B	96	9701	224	4126
14 B	4950	0	0	0
15 B	0	4950	0	0
16 B	0	0	0	0

**Table 2**  
**Results Obtained with Set of Calibration Samples**

SAMPLE NUMBER	mg/kg COPPER		mg/kg ZINC		mg/kg ARSENIC		mg/kg LEAD	
	GIVEN	MEASURED	GIVEN	MEASURED	GIVEN	MEASURED	GIVEN	MEASURED
1 B	4790	4854	4790	4784	6790	6815	980	946
2 B	0	31	0	0	11340	10870	0	227
3 B	0	207	0	187	0	145	4980	5267
4 B	9530	9895	95	7	9330	9372	95	153
5 B	8160	7757	240	416	7740	7792	240	192
6 B	6300	6112	482	495	5590	5324	484	611
7 B	3810	3848	1900	1806	11070	10620	4760	4927
8 B	2950	3161	983	1044	4530	4684	1474	1790
9 B	982	1097	2970	2938	3390	3496	1990	1999
10 B	1960	2034	3910	3712	2250	2142	2930	2939
11 B	490	638	6360	6261	1140	1057	2440	2379
12 B	243	635	8270	8354	565	367	3405	3594
13 B	96	392	9701	9571	224	52	4126	4163
14 B	4950	4940	0	141	0	0	0	68
15 B	0	128	4950	4928	0	0	0	130
16 B	0	67	0	31	0	0	0	31
RMS ERROR AROUND CALIB. CURVE	± 130		± 130		± 200		± 130	
COUNTING STA- TISTICS ERROR	± 20 to ± 30		± 15 to ± 20		± 20 to ± 40		± 30 to ± 50	
REPEATABILITY (PRECISION)	± 40		± 25		± 60		± 55	
ERROR DUE TO HETEROGENSITY OF SAMPLE (ON SAMPLE 10 B)	± 75		± 70		± 50		± 70	

NOTES—ALL VALUES IN [mg/kg].

—ALL MEASUREMENT TAKEN FOR 200 SEC. EACH.

spiking, each 100g. sample was homogenized by tumbling in its container for 2 hrs.

#### *Characterization of samples*

The quality of the synthetic calibration samples was tested on a high resolution laboratory x-ray spectrometer equipped with a Si/Li detector and Cd-109 radioactive source. A suite of ten 7g. aliquot was prepared from each 100g-sample. The aliquot were run on the spectrometer for 200 sec. each, and the x-ray intensities of the analytes Cu, Zn, As and Pb were measured.

In order to assess the intrinsic heterogeneity of the soil matrix, the x-ray intensity of iron was measured for each aliquot. Iron was selected: (1) for its relatively high concentration in the soil matrix (estimated at  $1.5 \pm .2\%$ ) and (2) because it is not one of the spiking elements, its concentration would remain undisturbed. Moreover, no significant spectral or matrix interferences on the iron x-ray intensity are expected. The ratio of the standard deviation of a series of all iron intensities measured to the overall mean iron intensity was used as a criterion of intrinsic heterogeneity of the soil matrix. This value, after being corrected for counting statistics error was found to be 2.3% relative.

In a similar manner, the dispersion of the spiking elements within

each 100g-sample was estimated by taking for each analyte the ratio of the standard deviation obtained on a series of 10 aliquot to the mean intensity for the set. This ratio varied between the spiking elements from 5.3 to 6.5% relative for all except one sample (9B).

This degree of homogeneity is considered to be entirely satisfactory for calibration of a rapid screening method, especially in view of the variability to be expected in the unprocessed soil that is being tested, where short range concentration variations as high as 200% are not uncommon.

## RESULTS

### *Analysis of Errors*

The applicability of synthetic samples described was evaluated by using them for calibration of a commercially available portable x-ray analyzer and subsequent analysis of unknown samples, also analyzed by an independent method.

The analyzer used was a standard X-MET 840 portable X-ray Analyzer equipped with a 100mCi curium 244 radioactive source in a rugged laboratory probe. The probe was fitted with a high resolution Xe/CO<sub>2</sub> gas filled proportional detector which is standard for this probe. A detailed description of the system can be found

**Table 3**  
**Results Obtained with Unknown Samples,**  
**Analyzed by Referee Method**

SAMPLE NUMBER	mg/kg COPPER		mg/kg ZINC		mg/kg ARSENIC		mg/kg LEAD	
	GIVEN	MEASURED	GIVEN	MEASURED	GIVEN	MEASURED	GIVEN	MEASURED
25 D	6730	5701	6150	4750	2640	2592	1600	1824
27 D	9580	8108	7880	6067	2460	2240	1610	1580
28 D	9970	8049	8180	6183	2820	2418	2090	1962
31 D	5240	4302	5600	4123	2940	3018	1970	2513
33 D	12800	10630	11800	9023	4080	2463	2910	1551
39 D	6480	5723	7630	6350	2170	2556	1630	2423
43 D	7600	6387	5850	4466	3240	2432	1930	1389

NOTE: ERRORS SEE TABLE 2.

elsewhere<sup>9</sup>.

The system was set up to record the x-ray intensities of Cu, Zn, As, Pb and also Fe, Rb and backscattered radiation. Each synthetic calibration sample was measured for 200 sec, and the net x-ray intensities of these elements were stored in the analyzer memory. For measurement, each sample was placed in a cup with a 6.2  $\mu$ -thick polypropylene film bottom (the x-ray exit and entrance window). The concentrations of spiking elements were entered into the instrument's memory and optimum calibration equations for each analyte were derived using the resident software. All calibration samples were then remeasured as unknowns and these results are listed in Table 2 along with other details of calibration.

The main sources of error listed in the Table are defined as follows:

- Counting statistics error, associated with any single measurement, represents the fluctuations due to the random nature of radiation and its interaction with matter.
- Repeatability, or precision, is expressed as one standard deviation of a series of at least ten consecutive measurements taken on the same, undisturbed sample. This value of standard deviation is usually greater than the counting statistics error, since it includes any short-term electronic fluctuations in the instrument.
- Error due to sample heterogeneity is obtained as one standard deviation of a series of at least 10 measurements taken on various aliquot of the same sample, corrected for repeatability error.
- The root-mean-square error (RMS) given in the table represents a spread of the experimental data around the calibration curve obtained by using the multivariable, linear least squares regression algorithm. The RMS error encompasses all the errors listed above plus those carried by the referee analysis. Therefore, to some degree, it may be regarded as a measure of the overall accuracy of the method.

The data in Table 2 allow one to determine the detection limit for each analyte defined here as three standard deviations of counting statistics obtained on a blank sample. The appropriate values for detection limit are  $\pm 90$  mg/kg Cu,  $\pm 60$  mg/kg Zn,  $\pm 120$

mg/kg As and  $\pm 150$  mg/kg Pb. Therefore, some values reported in Table 2 should be listed as below detection limit. They are reported here for the sake of completeness.

#### *Unknown samples*

Table 3 lists the results of measurements obtained on unknown samples of contaminated soil with the X-MET 840 calibrated with the suite of synthetic samples. These samples were analyzed as received. That is, all sampling, preparation, processing (grinding) and referee analyses were performed by an independent party. It is seen that the XRF results for Cu, Zn and As are systematically lower than those by the referee analysis, whereas the lead results do not show such a tendency. Ratios of measured to expected (referee) concentration values seem to vary around 0.8 for Cu and Zn, and about 0.9 for As. However, the results can still be qualified as satisfactory in terms of screening analysis which allows for an overall accuracy of  $\pm 50\%$  relative<sup>10,11</sup>.

Closer examination of the unknown samples pointed to particle size as the most likely cause of the difference. Indeed, the soil in the unknown samples appeared finer than the soil in the calibration samples.

To verify this possibility, approximately 0.5 kg. of previously prepared soil finer than 8 mesh was passed through a 100 mesh sieve. The fraction finer than 100 mesh was used to prepare an additional set of three 100g-samples, each spiked three different concentrations of copper and zinc in the range 0 to 5000 mg/kg. These samples were prepared and homogenized in precisely the same way as the original set of calibration samples.

These samples then were analyzed using the calibration developed with the original synthetic calibration samples. The concentrations of copper and zinc in all three samples were equal to 0.9 of the expected values, thus confirming the initial hypothesis.

#### **CONCLUSIONS**

It has been shown that spiked samples of natural soil are suitable for calibration of portable x-ray analyzers for screening analysis of hazardous waste. The calibration samples are prepared in a way



that assures their chemical and physical compatibility with the real samples of hazardous waste contaminated soil. The proposed method for analysis of hazardous waste samples with portable x-ray analyzers does not in any way upset the already accepted protocols for sampling and analysis. On the contrary, it complements them. The feasibility of calibration of portable x-ray analyzers with synthetic soil samples makes the on-site screening of hazardous waste a viable and realistic alternative to the prospect of risky selective sampling, costly laboratory analysis and delays.

With the option of a properly calibrated x-ray analyzer, the analyst can afford to do many more screening analyses on-site and define the hot zones more accurately, selecting for confirming analysis only the minimum necessary number of samples.

With the new calibration samples, grinding of soil samples is neither recommended nor necessary as coarse (below 8 mesh) material already provides results of sufficient accuracy.

While we feel that the results presented here are very encouraging and represent a breakthrough, there is room for further work. An interlaboratory comparison of the synthetic calibration samples is recommended. Furthermore, preparation of samples with elements other than Cu, Zn, As and Pb should be done forthwith.

#### REFERENCES

1. Furst G.A., Tillinghast V. and Spittler T., "Screening for Metals at Hazardous Waste Sites: A Rapid Cost-Effective Technique Using X-ray Fluorescence", *Proc. Natl. Conf. on Management of Uncontrolled Hazardous Waste Sites*, Washington, D.C., pp. 93-96, HMCRI, Silver Spring, MD 1985.
2. Tertian R. and Claisse F., *Principles of Quantitative X-ray Fluorescence Analysis*, Heyden and Son Ltd., 1982.
3. Jenkins R., Gould R.W. and Gedcke D., *Quantitative X-ray Spectrometry*, Marcel Dekker, Inc., New York, NY, 1981.
4. Berry P.F., "Developments in Design and Application of Field portable XRF Instruments for On-Site Alloy Identification and Analysis", presented at the 40th ASNT National Fall Conference, Atlanta, GA, Oct., 1981.
5. Woldseth R. and Meyer G.W., "Multielement Quality Control", *Indus. Res. and Dev.*, June 1978.
6. Jarvinen J.-L. and Sipila H., "Effects of Pressure and Admixture of Neon Penning Mixtures on Proportional Counter Resolution", *Nucl. Instr. Meth.* 193 (1982), pp 53-56.
7. Von Althaus C., Rautala P. and Rhodes J.R., "Applications of a New Multielement Portable X-ray Spectrometer to Material Analysis", *Adv. in X-ray Analysis*, 23, pp 27-36, 1980.
8. Berry P.F., Furuta T. and Rhodes J.R., "Particle Size Effects in Radioisotope X-ray Spectrometry", *Adv. in X-ray Analysis*, 12, pp 612-632, 1969.
9. Piorek, S. and Rhodes J.R., "Application of a Microprocessor Based portable Analyzer to Rapid Nondestructive Alloy Identification", *Advances in Instrumentation*, 41, Part 3, pp 1355-1368, ISA, 1986.
10. Raab G.A., Cardenas D., Simon S.J. and Eccles L.A., "Evaluation of a Prototype Field-portable X-ray Fluorescence System for Hazardous Waste Screening", U.S. EPA Report, pre-issue copy, August, 1987.
11. Chappell R.W., Davis A.O. and Olsen R.L., "Portable X-ray Fluorescence as a Screening Tool for Analysis of Heavy Metals in Soils and Mine Wastes", *Proc. Natl. Conf. on Management of Uncontrolled Hazardous Waste Sites*, Washington, D.C., pp 115-119, HMCRI, Silver Spring, MD 1986.

# Portable X-Ray Fluorescence as a Screening Tool for Analysis of Heavy Metals in Soils and Mine Wastes

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## ABSTRACT

X-ray fluorescence (XRF) has several advantages over atomic absorption and inductively coupled plasma techniques that make it useful for the screening analyses of environmental samples. These advantages are: rapid turnaround time, multi-element analytical capacity, nondestructive analyses, minimal quantity of sample required and cost-effectiveness. Further, a portable XRF instrument has the capability of providing on-site analyses that can be incorporated immediately into the field investigation program. The realization of the potential of a portable XRF device has led to an increase in its use in remedial investigations at hazardous waste sites. In most cases, however, the accuracy and precision of the analyses, along with the method detection limits, have not been well characterized. In this paper, these parameters are established for a variety of soil/tailings matrices, calibration techniques and field situations.

The authors have used a portable XRF analyzer to determine heavy metals concentrations in soils, sediments and mining wastes at three hazardous waste sites in Colorado and Montana. The elements determined using a Columbia Scientific portable XRF analyzer were lead, arsenic, copper, zinc and iron. These three sites represent several potential applications of XRF analyses, including: (1) on-site selection of sample locations necessary for definition of contaminant boundaries, (2) screening of samples for further analyses through the Contract Laboratory Program (CLP) and (3) statistical and geochemical evaluation of the spatial variation of metals concentrations. The requirements and limitations of XRF analyses for each application are evaluated.

The results obtained substantiate the dependence of method detection limits on sample matrix variability and analyte concentration ranges. The accuracy and precision of the analytical technique also depend on the number and type of calibration standards used. These conclusions are demonstrated by statistical evaluation of the results of the calibration for combinations of 5, 10, 15 and 20 standards. The results of both replicate analyses and XRF versus CLP comparisons are presented and are used to determine potential sources of error and their relative magnitudes for the entire procedure. This knowledge can be directly applied to the design of field programs that more effectively meet the accuracy, precision and detection limit requirements of XRF analyses for remedial investigations at hazardous waste sites.

## INTRODUCTION

As part of the remedial investigations at three hazardous waste mining sites, screening for heavy metals contamination was performed with the aid of a portable energy dispersive X-ray fluorescence (XRF) analyzer. At Site A in Colorado, definition of a 1,000 mg/kg Pb isopleth using on-site XRF in conjunction with

geostatistics was accomplished.<sup>1</sup> In the identification of hotspots and areas requiring further investigation at Site B in Montana, XRF provided a useful and cost-effective method for screening for As, Pb, Cu and Zn. XRF screening also was utilized to select samples for further analysis through the Contract Laboratory Program (CLP). At Site C in Colorado, analyses for Pb, As, Cu, Zn and Fe in split spoon tailings samples provided additional information on the relationships between degree and depth of contamination. In this way, zones of metal accumulation and leached zones of metal depletion could be identified.

The potential use of XRF spectrometry as a screening technique for trace constituents at hazardous waste sites has been demonstrated by several studies.<sup>2,3</sup> In these cases, however, analyses were performed by dedicated laboratory instruments employing sophisticated computer software. The additional advantage of immediate results has led to an increased interest in portable XRF systems, which necessarily are less sophisticated. The purpose of this study was to outline the techniques essential to the proper use of portable XRF instruments and to evaluate the results obtained in relation to the designed screening use of the method.

## XRF THEORY

The fundamental principle of X-ray fluorescence (XRF) or emission spectrometry is the detection and measurement of the X-rays emitted from excited atoms in a sample. The excited state is achieved when the critical binding energy of an electron in a particular shell is exceeded by the energy of the incoming source particle. When this happens, an orbital electron is removed from the shell (the atom is ionized) and another electron from a higher energy shell takes its place. The excess energy released as an X-ray photon during this process is characteristic of the atom from which it was produced. There are, of course, many complications to this simplified discussion of XRF theory, and a vast amount of literature addresses them in detail.<sup>4,7</sup>

Two general types of emission spectrometers can be used: wavelength dispersive (WD) and energy dispersive (ED). Wavelength dispersive systems normally provide very high resolution (sharp narrow peaks) but, because of the additional diffraction step, they suffer from low efficiency (the energies of the characteristic X-rays are attenuated by the diffraction process). Energy dispersive systems, on the other hand, are highly efficient but have less resolving power. Because ED spectrometers do not require high source energies for excitation (i.e., they are more efficient) and elaborate mechanisms for geometric positioning of the detector, they are more adaptable for use in the field. Several compact ED systems are now available, some with sophisticated software capabilities.

The energy dispersive XRF system used in this study was a Columbia Scientific X-MET 840 portable analyzer. The X-MET 840 employs a radioisotope source for sample excitation and a high resolution proportional counter for X-ray detection. For the elements analyzed for in this study (Pb, As, Cu, Zn and Fe), a 100 millicurie source, composed of Cm 244 which emits Pu L X-rays with energy ranging from 12 to 20 KeV, was used. The resolution of the spectrometer, as defined by the full width at half the maximum (fwhm) height of the Mn K alpha peak at 5.9 KeV, is about 0.83 KeV or 14%. Typical laboratory ED instruments are now capable of resolutions of less than 0.15 KeV or 2.5%.

## SAMPLE MATRIX EFFECTS

The most important consideration in the measurement of X-ray energy is the influence of sample matrix effects. Matrix effects can either increase or decrease characteristic X-ray intensities and, if not corrected for, can lead to significant accuracy problems. In general, these effects can be divided into either physical or chemical matrix effects.

Physical matrix effects are the result of variations in the physical character of a sample. They may include such parameters as particle size, uniformity, homogeneity and surface condition. For example, consider a sample in which the analyte exists as very fine particles within a matrix composed of much coarser material. If two separate specimens (aliquots) of the sample are ground in such a way that the matrix particles in one are much larger than in the other, then the relative volumes occupied by the analyte-containing particles will be different in each. When measured, a larger amount of the analyte will be exposed to the source X-rays in the specimen containing larger matrix particles, resulting in a higher intensity reading for that specimen.

Chemical matrix effects result from differences in concentrations of interfering elements. These effects appear as either spectral interferences (peak overlaps) or as absorption/enhancement phenomena. Both effects are common in soils contaminated with heavy metals. For example, Fe tends to absorb Cu K X-rays, reducing the intensity measured by the detector. This effect can be corrected if the relationship between Fe absorption and X-ray intensity can be modeled mathematically. Obviously, establishment of all matrix relationships during the time of instrument calibration is critical.

Sample matrix effects can never be fully eliminated. They can become relatively insignificant, however, through proper sample preparation and calibration techniques. The techniques used in this study are addressed more fully in the following section.

## METHODOLOGY

### Sample Preparation

Samples to be analyzed by XRF (including calibration samples) were placed in aluminum pans, air-dried and mixed as well as possible. A representative portion of each sample (40-100 g) was ground to less than 100 mesh, and a 5-10 g aliquot of the resulting powder was then analyzed with the spectrometer. Sample preparation time averaged between 10 and 15 min/sample. Actual analysis time was 4 min/sample.

By saturating the sample preparation step, analytical variations due to physical matrix effects were minimized. In other words, although the physical characteristics of the samples may have been affecting the intensities of X-rays, correction for these effects was not necessary because they were the same for all samples. Of course this assumption was valid only for samples with identical or at least very similar matrices (e.g., for samples collected from the same site). Although the assumption was reasonable from a theoretical standpoint, in practice it was difficult to test. However, one important aspect, homogeneity of the

ground powder, was tested. The results of this determination are evaluated later in this paper.

### Calibration

The calibration of the XRF spectrometer was based on previously collected and analyzed samples from each site. These samples were handled with the same procedures outlined above in "Sample Preparation." After digestion with  $\text{HNO}_3/\text{H}_2\text{O}_2$  according to the procedures specified by the CLP, samples were analyzed by either inductively coupled plasma (ICP) or atomic absorption (AA) techniques by different laboratories with CLP procedures. The samples do not represent "true" calibration standards in the sense that the accuracy of the different CLP laboratories was not beyond repute. Nevertheless, the potential calibration error due to the inaccurately known concentrations in the samples was probably much less than the potential matrix effect errors that would result using "true" standards with unknown matrices.

Calibration was accomplished by first measuring the intensities of the characteristic analyte X-rays, then developing a concentration versus net intensity regression curve. The calibrations employed for each element and for each site were essentially mathematical models designed to compensate for sample matrix effects specific to the site. The goal was to optimize the calibration for each analyte by correcting for both spectral overlap and/or element interference, if necessary. Spectral overlap, which occurs when two peaks are not completely resolved, was removed by deconvolution (subtraction of one peak intensity from that of another). Absorption or enhancement of characteristic X-rays due to the presence of interfering elements was handled by multiple linear regression analysis. All of the software necessary for calibration is contained within the instrument.

Table 1 summarizes the results of the calibration obtained for each element at each site. The table provides the number of calibration standards (n), the range of concentrations in the standards, the instrument detection limit (discussed in next section) and the resulting correlation coefficient. In all cases, the calibration was excellent with correlation coefficients typically greater than 0.95.

Table 1  
XRF Calibration Parameters

Site	Element	n	Analytical Range (ng/kg)	SD <sup>1</sup> (ng/kg)	Correlation Coefficient (R)	IDL <sup>3</sup> (ng/kg)
Site A	Pb	3	0-1,000	38	0.999	120
Site B	Pb	20	0-1,200	97	0.949	75
	As	16	0-1,700	91	0.963	90
	Cu	18	0-2,200	190	0.963	60
	Zn	20	0-2,500	267	0.943	30
Site C <sup>2</sup>	Pb	20	0-4,800	425	0.933	45
	As	20	0-250	20	0.963	15
	Cu	20	0-3,900	137	0.991	90
	Zn	20	0-5,400	97	0.997	60
	Fe	20	0-180,000	18,200	0.931	140

1 Overall standard deviation (root mean square of the residuals) for the regression

2 Model #5 (20 calibration samples)

3 Instrument detection limit

### ANALYTICAL PRECISION

Replicate analyses were performed to determine the analytical precision of the X-MET 840. For each site, a check sample was analyzed at regular intervals throughout the analytical run. The results, shown in Table 2, include both instrumental error and error due to spectrometer drift. The data indicate that replicate



precision (as indicated by CV, coefficient of variance or standard deviation divided by the mean) is generally less than  $\pm 20\%$  for concentrations approaching the method detection limit. At higher concentrations, however, precision is generally less than  $\pm 5\%$ .

Table 2  
XRF Replicate Precision

Site	Element	n	Mean (mg/kg)	SD (mg/kg)	CV (%)	MDL (mg/kg) <sup>1</sup>
Site A	Pb	93	409	52	12.7	156
Site B	Pb	16	143	32	22.4	96
	As	16	215	33	15.3	99
	Cu	16	846	21	2.5	63
	Zn	16	550	17	3.1	51
Site C <sup>2</sup>	Pb	35	713	14	2.8	42
	As	35	51	7	12.9	21
	Cu	35	597	27	4.5	81
	Zn	35	728	20	2.8	60
	Fe	35	13,800	870	6.3	2,610

<sup>1</sup> Method detection limit

<sup>2</sup> Model #5 (20 calibration samples)

### XRF DETECTION LIMITS

The limiting factor for XRF precision is the error associated with the X-ray counting process. This error results from the random nature in which X-rays are emitted from the radioisotope source, excited in the sample and counted by the detector. Thus, the lower limit of detection can be estimated from the standard deviation of the counting statistic. For this study, the instrument detection limit (IDL) of the spectrometer was calculated as three times the standard deviation of the counting statistic. It is important to note that the magnitude of the counting error, and thus the lower limit of detection, is directly related to both the total number of X-rays counted and the number of X-rays due to interference and background. Thus, the IDL varies as a function of both measurement time and sample matrix. For example, as shown in Table 1, the IDL for Pb at each site is 120 mg/kg (Site A), 75 mg/kg (Site B) and 45 mg/kg (Site C).

In a similar manner, the method detection limit (MDL) can be estimated from the replicate precision data (Table 2). As noted above, replicate measurements also include the error due to instrumental drift. A comparison of Table 2 with Table 1 indicates that, in general, MDLs are only slightly higher than IDLs, suggesting that instrumental drift was not a significant source of error for the XRF analyses.

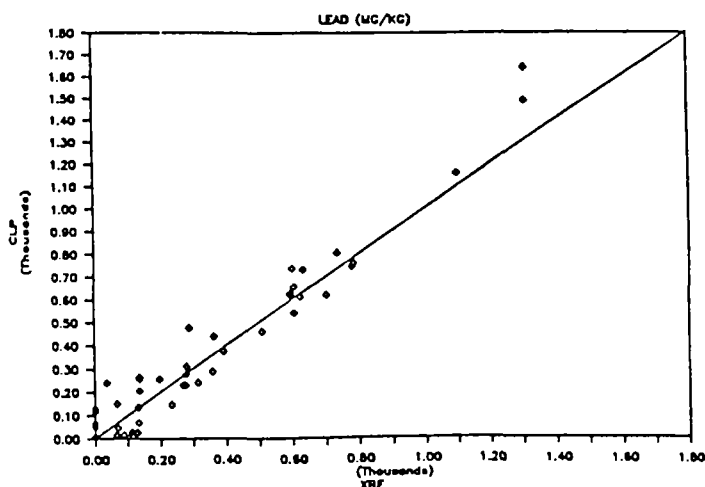


Figure 1  
XRF vs. CLP for Pb in Site B Soil Samples

### XRF VERSUS TRADITIONAL METHODS: STATISTICAL TESTS ON PAIRED DATA

Following XRF analyses at each site, a selected number of ground specimens were sent to the U.S. EPA's CLP for confirmatory analyses. These samples were analyzed by either ICP or AA methods. The results obtained were then compared to the XRF results in order to evaluate the adequacy of the XRF method.

Figs. 1 through 5 are examples of the scatter diagrams obtained for XRF versus CLP analyses. To better evaluate the degree of fit of the data, statistical parameters were calculated. The results of these analyses are given in Table 3 and include the average relative deviation (d), relative standard deviation (Sd), t and Wilcoxon test statistic and the corresponding two-tailed t-test and Wilcoxon test critical values at the 95% confidence level. Readings below the MDL and significant outliers were not included in the statistical analysis.

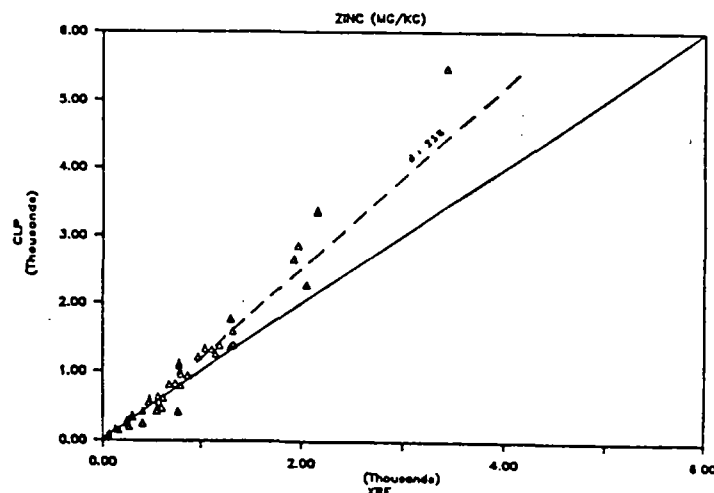


Figure 2  
XRF vs. CLP for Zn in Site B Soil Samples

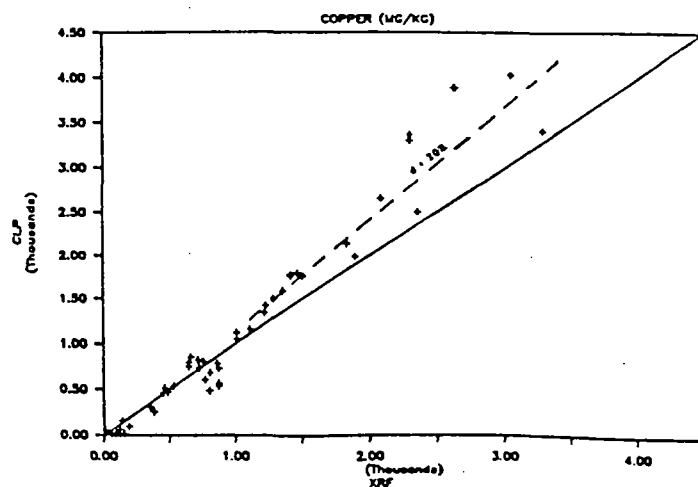


Figure 3  
XRF vs. CLP for Cu in Site B Soil Samples

The average relative deviation (d) represents the degree of deviation of the data from a one-to-one correlation. For example, as illustrated in Fig. 2, the XRF versus CLP results show a positive deviation of about 25% (dashed line) from perfect agree-

ment (solid diagonal line) for Zn concentrations above approximately 1,000 mg/kg. Such deviations are probably the result of uncorrected matrix effects due to an inadequate number of calibration samples at higher concentrations. Below 1,000 mg/kg, the average relative deviation is 0% (see Table 3 and Fig. 2).

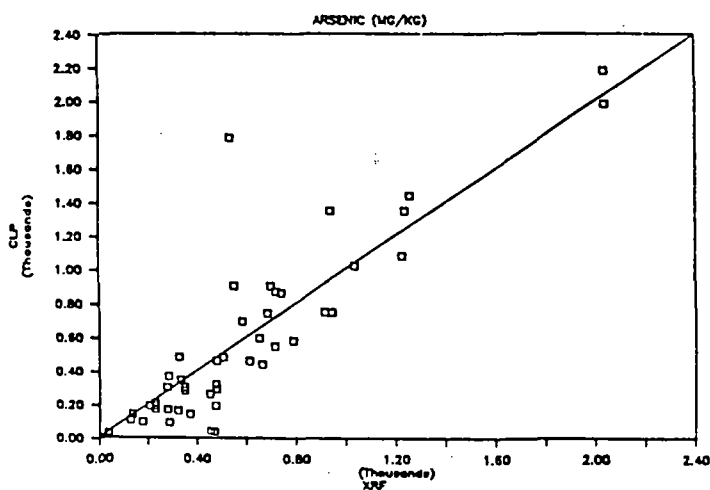


Figure 4  
XRF vs. CLP for As in Site B Soil Samples

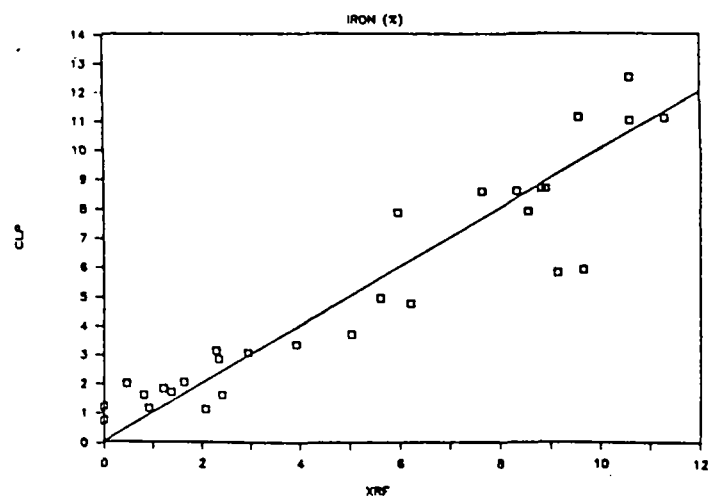


Figure 5  
XRF vs. CLP for Fe in Site C Tailings Samples

The agreement between the XRF and CLP results was evaluated using Student's t-test and Wilcoxon's signed-rank test. The t-test determines whether the means of two normally distributed populations are the same, while the Wilcoxon test determines whether two populations are symmetric (same or similar shapes) and, if symmetric, whether they differ in location. Since normal distributions also are symmetric, the Wilcoxon test is probably the preferred test.<sup>8</sup> The Wilcoxon test typically is termed a non-parametric or distribution-free test while the t-test is appropriate only for normally distributed data.

Through statistical analyses, it was determined that, for all elements, neither the CLP nor the XRF data were distributed normally. Rather, the populations more closely resembled log-normal symmetric distributions. Further, most element distributions were bimodal. Therefore, the t-test was applied to the log-transformed data, and the Wilcoxon test was applied to the non-

Table 3  
X-MET and CLP Comparison

Site	Parameter	Range (mg/kg)	n	d (Z)	Sd (Z)	Wilcoxon Test			t-Test	
						W-	W+	W.95	t	t.95
Site B	As	34 - 2180	45	-15	34	664	371	344	-0.90	2.01
	Cu	64 - 1340 1340 - 1030	26 16	-9 70	26 11	193 0*	159 136	98 30*	-1.77 4.73*	2.06 2.11*
	Pb	69 - 1640	33	4	36	203	358	171	0.99	2.03
	Zn	34 - 1000 1000 - 3470	30 18	0 25	33 13	337 0*	213 171	137 41*	-0.04 9.64*	2.05 2.11*
	Fe	34 - 20,000	13	25	63	25	66	17	1.42	2.18
Site C <sup>1</sup>	Pb	15 - 2400	31	28	59	105*	391	148*	2.50*	2.04*
	As	0 - 131	31	15	88	211	290	148	1.37	2.04
	Cu	0 - 1140	31	-16	127	202	295	148	-1.61	2.04
	Zn	70 - 2290	31	10	40	142*	354	148*	1.40	2.04
	Fe	0 - 150,000	31	2	62	276	270	148	0.17	2.04

1 Model 5 (20 Calibration Samples)

\* = significant difference

transformed data. The results given in Table 3 were evaluated as follows:

- Agreement between the XRF and CLP populations was indicated for values of t between  $\pm 1.95$ . Values of t outside of  $\pm 1.95$  indicated that the two population means were significantly different at the 95% confidence level.
- Agreement between the XRF and CLP populations was indicated for values of W.95 that fell outside of the critical range of W- and W+ (or both W- and W+ must be greater than W.95). For example, from Table 3, a value of W.95 = 171 is given for Site B Pb. Since this value lies outside of the W- = 203 and W+ = 358 range, the means of the two populations do not differ significantly at the 95% confidence level.

As indicated in Table 3 by the asterisk, both statistical tests indicate significant differences in the two methods only for Pb at Site C and Cu and Zn at Site B.

#### SIGNIFICANCE OF THE NUMBER OF CALIBRATION SAMPLES

To correct for absorption or enhancement interferences, an adequate number of calibration samples must be included in the regression model. The exact requirements will depend on the number of potentially interfering elements, their concentration range(s) and the requirements of the particular investigation. The greater the knowledge about how a sample matrix varies at a particular site, the more sophisticated the calibration model can be and, therefore, the more accurate the results.

To address the significance of the number of calibration samples, five different models were developed for Site C. Each model (1 through 5) covered similar analytical ranges but had pro-

Table 4  
Site C Zinc versus Number of Calibration

Model	Number of Calibration Samples	n	d (Z)	Sd (Z)	Wilcoxon Test			t-Test	
					W-	W+	W.95	t	t.95
1	5	31	-18	131	175	321	148	-1.78	2.04
2	10	31	16	66	122	376	148	0.30	2.04
3	15	31	16	74	127	360	148	0.32	2.04
4	20	31	19	38	101	393	148	2.71	2.04
5	20	31	10	40	142	354	148	1.40	2.04

gressively larger numbers of calibration samples. The results obtained for each model then were compared to the corresponding CLP results. As shown in Table 4, a significant improvement in the comparison for Zn occurred between model 1 (5 calibration samples) and model 2 (10 calibration samples), but the relative improvement became decreasingly less above 10 calibration samples. This same trend was observed for the other Site C elements and indicated that at least 10 calibration samples were necessary to adequately analyze the samples (i.e., to correct for the variation in matrix element concentrations), but more than 10 probably were not necessary.

## ANALYSIS OF VARIANCE

The purpose of this section is to address the various sources of error associated with the XRF analytical technique. The magnitude of these errors, as measured by their variances ( $S^2$ ), then can be evaluated for the statistical significance relative to the overall variance of each element (contaminant) within the sample environment. In this way, it is possible to determine whether or not the XRF technique can distinguish between different concentrations of an element within a contaminated area and, therefore, whether the technique is valid for screening analysis.

For this determination, total variance was broken down into three components, as shown by:

$$S^2_{\text{Tot}} = S^2_{\text{Sample}} + S^2_{\text{Calib}} + S^2_{\text{Anal}} \quad (1)$$

where each variance component was evaluated as follows:

- Sample variance ( $S^2_{\text{sample}}$ ) was determined from the concentration distribution of the entire population.
- Calibration variance ( $S^2_{\text{Calib}}$ ) was determined from the standard deviation (SD) of the calibration curve (Table 1). This variance included both the error due to uncorrected matrix effects and the error due to the uncertainty in calibration sample concentrations.
- Analytical variance ( $S^2_{\text{Anal}}$ ) was determined from the standard deviations of both replicate precision (Table 2) and sample preparation. This variance included instrumental (counting) error, drift error and error due to the nonhomogeneity of the ground specimen.

Homogeneity was determined by analyzing separate aliquots of the ground specimen. The standard deviation obtained from the analysis was of the same order as that obtained for the replicate precision analyses. Therefore, the error due to powder nonhomogeneity was negligible for these samples.

The percentage of the total variance of each component is shown in Table 5; the variance due to the samples ( $S^2_{\text{Sample}}$ ) is by far the primary component in all cases. Calibration variance ( $S^2_{\text{Calib}}$ ) and analytical variance ( $S^2_{\text{Anal}}$ ) are relatively minor. This result indicates that the XRF technique is adequate for distinguishing between different concentrations of the contaminants at the three sites. In other words, the error due to the X-MET calibration and analysis is insignificant relative to the total variance of each element.

## CONCLUSIONS

The data presented in this study indicate that the portable X-ray fluorescence technique is suitable for screening As, Pb, Cu, Zn and Fe in soils contaminated with mine wastes. The XRF versus CLP comparisons show no statistically significant differences between the two analytical results for these elements over most concentration ranges. As determined by the components of variance analysis, the errors resulting from the XRF method are minor compared to the sample variance at each of the three sites. This result illustrates the ability of the XRF method to

discriminate between different contaminant levels under the highly variable concentration conditions likely to be encountered at mining waste sites.

Table 5  
Analysis of Variance

Site	Element	Percent of Total Variance		
		$S^2_{\text{Sample}}$	$S^2_{\text{Calib.}}$	$S^2_{\text{Anal.}}$
Site A	Pb	100	0	0
Site B	Pb	90	9	1
	As	94	5	1
	Cu	95	4	1
	Zn	86	14	1
Site C <sup>1</sup>	Pb	76	24	0
	As	64	19	17
	Cu	87	12	1
	Zn	98	2	0
	Fe	99	1	0

<sup>1</sup> Model 5 (20 Calibration Samples)

The results confirm the importance of obtaining an adequate number of calibration samples in order to model the matrix variations present within the samples. For Site C, at least 10 calibration samples were necessary to correct for sample matrix effects. Although more than 10 samples did further improve the calibration, the degree of improvement was not significant, especially in light of the intended screening use of the XRF technique.

For the three sites discussed in this paper, a total of about 1,000 soil/tailings samples have been analyzed with the X-MET 840 X-ray fluorescence analyzer. These analyses have helped establish heavy metal relationships, including both the spatial extent and relative degree of contamination. The ease of sample preparation and analysis in the field (i.e., rapid turnaround times) has been invaluable for on-site coordination of field sampling activities. Also, selection of more representative sample sets for further CLP characterization has been achieved. These advantages have made XRF screening for heavy metals a very cost-effective means of maximizing the amount of information obtained from a field sampling campaign.

## REFERENCES

1. Mernitz, S. and Olsen, R., "Use of Portable X-ray Analyzer and Geostatistical Methods to Detect and Evaluate Hazardous Materials in Mine/Mill Tailings," *Proc. National Conference on Management of Uncontrolled Hazardous Waste Sites*, Washington, DC, 1985, 107-111.
2. Furst, G.A., Tillinghast, V. and Spittler, T., "Screening for Metals at Hazardous Waste Sites: A Rapid Cost-Effective Technique Using X-ray Fluorescence," *Proc. National Conference on Management of Uncontrolled Hazardous Waste Sites*, Washington, DC, 1985, 93-96.
3. Kendall, Lowry, Bower and Mesnavos, "A Comparison of Trace Metal Determinations in Contaminated Soils by XRF and ICAP Spectroscopies," U.S. EPA National Enforcement Investigations Center.
4. Russ, J.C., *Fundamentals of Energy Dispersive X-ray Analysis*, Butterworths and Co., Ltd., 1984, 308.
5. Jenkins, R., Gould, R.W. and Gedcke, D., *Quantitative X-ray Spectrometry*, Marcel Dekker, Inc., New York, NY, 1981, 586.
6. Tertian, R. and Caisse, F., *Principles of Quantitative X-ray Fluorescence Analysis*, Heydon and Son Ltd., 1982, 385.
7. Dzuby, T.G. Ed., *X-ray Fluorescence Analysis of Environmental Samples*, Ann Arbor Science, Ann Arbor, MI, 1977, 310.
8. Bradley, J.V., *Distribution-Free Statistical Tests*, Prentice-Hall, New York, NY, 1968, 388.

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Superfund

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# Data Quality Objectives for Remedial Response Activities

## Example Scenario:

### RI/FS Activities at a Site with Contaminated Soils and Ground Water

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As part of the data analysis the uncertainty surrounding the estimate of the mean contaminant concentration within the depressed area will be determined. Determining this uncertainty requires knowledge of the spatial variability of the data as a function of distance (see Appendix A Development Process manual). To model spatial variability, data separated by small and large distances are required; thus, the hybrid grid is ideal for determining spatial variability as a function of distance.

### 5.3.5 EVALUATE SAMPLING/ANALYSIS OPTIONS: RI PHASE IC - SURFACE SOIL INVESTIGATIONS

Analysis options include CLP, local laboratory, and on-site analysis. Each type of analyses has certain properties which are presented below.

<u>Analytical Method</u>	<u>Turnaround Time</u>	<u>Cost per Sample</u>	<u>Relative Accuracy And Precision</u>
CLP/RAS	6 weeks <sup>a</sup>	\$60 <sup>b</sup>	High
Local Lab/SAS <sup>e</sup>	2-7 days	\$80 <sup>c</sup>	High
On-Site Analysis	2-24 hours	\$ 8 <sup>d</sup>	Unknown

- a. Time includes data validation.
- b. Cost is for paperwork and shipping only. No lab cost is included.
- c. Atomic absorption, acid digestion analysis cost. Includes paperwork cost.
- d. Cost is for sample preparation and analysis labor only.
- e. Costs for SAS are similar to b above.

Because future phases of this study depend on the results of this phase, the turnaround time of an analytical method is a critical issue. If the CLP is used to analyze these samples, project delays may be unavoidable. Both the local lab and on-site analysis provide adequate turnaround times, however, on-site analysis is 10 times less expensive than the local lab. Thus, on-site analysis would allow 10 times more samples to be analyzed at the same cost as local lab analysis.

Based on known site history and the conceptual model (see Section 5.3.4) a large number of samples will be required to characterize the extent of contamination. The only available analytical method which can be used to analyze a large number of samples for an acceptable cost is on-site analysis. The on-site analysis method of choice is X-ray fluorescence using a Columbia Scientific X-Met 840 (X-Met) or similar instrument.

Ordinarily on-site (Level II) analysis would not be suitable for risk assessment uses. However, in this case, a rigorous field calibration procedure with off-site laboratory verification of the calibration standards will be used. Also, a large number of QC samples will be analyzed to estimate precision and accuracy. The resulting data will be statistically reviewed and, if the field data are judged unreliable, the soil samples will be sent to an off-site laboratory for analysis. The use of these procedures makes this field analysis more like a Level III analysis and, therefore, suitable for risk assessment uses.

Experience with the X-Met at previous sites indicates that the detection limit of the X-Met ranges from 2 to 200 mg/kg. Based on these values the X-Met might not provide adequate detection limits; however, consultations with experts on the method indicate that there is high likelihood that the X-Met will provide detection limits less than 20 mg/kg. To allow for the possibility that the detection limits of

Outside the boundary of the source area, TCE was the only compound detected in appreciable concentrations. The presence of volatile organics in the soil gas outside the bounds of the soil depression may be indicative of the movement of the ground water plume in an easterly direction.

The results of Phase I soil gas sampling indicate a need to obtain additional soil samples (at depth) in order to determine the extent of soil contamination. Samples of ground water encountered within the area delineated by the soil gas plume should also be obtained to determine if the soil gas plume data can be correlated to the ground water contaminant levels.

### 5.5.3 ANALYSIS OF RESULTS: RI PHASE IC - SURFACE SOIL SAMPLING

#### 5.5.3.1 Calibration of X-Met (Precision and Accuracy achieved for metals analysis)

To calibrate the X-Met, four calibration samples were taken along a radial line from the center of the depressed area. The sample locations were shown in Figure 5-4. Each of the four samples was split into seven replicate samples as shown in Figure 5-5. Four replicates from each sample or 16 samples were sent to a local lab with an in-place QA/QC program and were analyzed for lead, chromium, and arsenic. Only the results for the lead samples are discussed here since the analysis performed for the other elements is analogous. Table 5-7 summarizes the results for lead.

The average of the four replicate analyses was taken as the actual value for each of the four calibration samples and the X-Met was calibrated using these values. During analyses of actual samples, each of the calibration samples were run 15 times. Based on the X-Met analyses of the replicates, the accuracy and precision can be expressed as a function of concentration. Accuracy will be expressed in terms of bias where bias is expressed as:

$$\text{Bias} = \frac{\bar{X} - A}{A}$$

Where:

$\bar{X}$  is the mean of the 15 replicates, and

A is the concentration determined from samples sent to the local lab.

Precision will be expressed as the standard deviation of the 15 replicates. The accuracy and precision of the X-Met are presented in Table 5-8.

Table 5-8 shows that the X-Met has accuracy values which are within  $\pm 10$  percent over the entire range of concentration. This is an acceptable accuracy value and indicates that the X-Met should, on average, accurately reproduce the contaminant levels throughout the site.

Given the accuracy and precision of the X-Met analyses, the detection limit for the method can be determined. When the X-Met results are reported, it is extremely unlikely that the reported values will be exactly equal to the actual value. This analytical error is expected and acceptable; however, it is generally not acceptable to report a positive concentration for a compound when, in fact, the compound is not present in the sample. The use of a detection limit lowers the risk of this occurrence to an acceptable level. For X-Met analyses (lead in this case), the detection limit will be set so that when a value is reported above the detection limit, there will be greater than a 99 percent chance that lead is actually present in the sample.

**TABLE 5-7**  
**RESULTS OF REPLICATE ANALYSES FOR LEAD (CALIBRATION SAMPLES)**

<u>SAMPLE #</u>	<u>REPLICATE #</u>				<u>MEAN</u>	<u>S.D.</u>
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>		
1	178	171	192	183	181	8.8
2	811	777	820	840	812	26.3
3	263	287	242	277	267	19.3
4	5	4	8	6	5.8	1.7

ALL UNITS IN mg/kg

S.D. = STANDARD DEVIATION

**TABLE 5-8**  
**ACCURACY AND PRECISION OF THE X-MET**  
**(Results of Lead Analysis- mg/kg)**

CALIBRATION SAMPLE #	PB CONCENTRATION (LOCAL LAB)	MEAN X-MET CONCENTRATION	ACCURACY	PRECISION	PRECISION/MEAN
4	5.8	5.5	-.05	2.7	.46
1	181	162	-.10	6.2	.03
3	267	278	.04	7.2	.03
2	812	800	-.02	14.0	.02



The detection limit will be based on the distribution of analytical errors. In this example, the distribution of analytical errors is the distribution of errors for calibration sample #4. This sample was chosen since it has the lowest concentration of lead and is therefore most representative of the performance of the X-Met at low concentrations.

The distribution of the 15 replicates of calibration sample #4 is normal, with a mean of 5.5 mg/kg and a standard deviation of 2.4 mg/kg. The actual concentration of sample #4 is 5.0 mg/kg. Thus the average error is 0.5 mg/kg and the distribution of errors is normal, with a mean of 0.5 mg/kg and a standard deviation of 2.4.

Based on the above assumption, the detection limit can be determined as:

$$\Pr(Z < D) \geq 99\%$$

where Z is an error  
D is the detection limit

Since the errors are normally distributed, a normal probability table can be used to determine the detection limit D. The standard normal variable corresponding to 99% probability is 2.33 (see Table 5-9). The detection limit is then:

$$\frac{D - m}{s} = 2.33$$

where s is the standard deviation, and  
m is the average error

$$\frac{D - (-0.3)}{2.17} = 2.33$$

$$D = 5.99 \text{ mg/kg}$$

$$= 6.0 \text{ mg/kg}$$

So, if the X-Met reports greater than 6.0 mg/kg lead there is at least a 99 percent chance that lead is present in the sample. If the X-Met reports less than 6 mg/kg, a value of 3 mg/kg will be used as an estimate of the concentration. A non-zero concentration is reported when lead is below the detection limit because lead is present to some degree in all surface soils. The value 3 mg/kg is attributed to soils with non-detectable lead concentrations because this value is thought to adequately represent the background lead concentration in the site area.

#### 5.5.3.2 Geostatistical Analysis of Surface Soil Sampling Results

Samples were collected and analyzed at each of the 89 locations on the hybrid grid. Samples were analyzed for lead, arsenic, and chromium. Only the results for lead are discussed here. The lead concentrations found at each sample location are shown in Figure 5-9. Contours of the data indicate that the proposed conceptual model for this site is incorrect. Contamination does not occur in small isolated pockets; rather, there are two large contaminated zones. The two contaminated zones are bounded by zones of undetectable lead contamination, so the horizontal extent of the contamination is known.

ARD Internal Report No. 356

IN SITU ANALYSIS OF WASTE WATER USING PORTABLE  
PRECONCENTRATION TECHNIQUES AND A PORTABLE XRF ANALYZER

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IN SITU ANALYSIS OF WASTE WATER USING PORTABLE  
PRECONCENTRATION TECHNIQUES AND A PORTABLE XRF ANALYZER

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ABSTRACT

The use of ion-exchange resin-loaded filter paper is described for collection and preconcentration of waste water samples in a form suitable for in-situ X-ray fluorescence analysis. Trace element determinations are performed using a new portable XRF instrument developed specifically for thin specimen measurements. Preconcentration of 150 ml samples on SA-2 ion-exchange paper followed by 100-second counting periods, per element, yields detection limits low enough for rapid, field monitoring of trace elements in waste water. Sample preparation time is less than 15 minutes.

INTRODUCTION

The combination of a field method for sample preconcentration with a portable X-ray fluorescence analyzer would make possible rapid, on-site monitoring of industrial waste waters for trace metals. A newly-developed Portable Elemental XRF Survey Meter is described elsewhere in these Proceedings (Rhodes, 1980). The purpose of the work reported here is to select and optimise a technique for preconcentration of waste water that can be used in field conditions with the portable XRF analyzer.

Many methods for preconcentration of trace elements in waters have been investigated (Rhodes, 1979). They include precipitation, co-precipitation, ion-exchange, silylation, liquid-liquid extraction, vapor filtration, evaporation, adsorption and electrodeposition. All these can be used in the laboratory but very few in the field. After a careful review of the properties and features of each method, we concluded that the one most suited to adaptation for field operation is the use of ion-exchange resin-loaded filter paper (Spano, 1966; Bergmann, 1967; Campbell, 1966 & 1970; and Law, 1973).

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between flow rate, number of recirculations and sample volume. The best solution pH must also be found. We used the same flow rate as Campbell and optimised the number of recirculations, the pH and the sample volume to match the sensitivity of the portable analyzer and the expected trace element concentrations in waste water (Biechler, 1965).

An aqueous solution (at pH = 1) of the following 14 ions was prepared:  $\text{Cr}^{+3}$ ,  $\text{Fe}^{+3}$ ,  $\text{Zn}^{+3}$ ,  $\text{Co}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ag}^{+1}$ ,  $\text{Cd}^{+2}$  and  $\text{Hg}^{+2}$ , each at a concentration of 1 mg/l, and  $\text{Ca}^{+2}$  at 4 mg/l. 50 ml aliquots of this solution were circulated through preconditioned SA-2 filter discs an increasing number of times, using new solution and a new filter for each recirculation test. After air drying, the filters were monitored using an energy dispersive X-ray spectrometer equipped with a Si (Li) detector and a Cd-109 source (Rhodes, 1972). The following characteristic X-rays were measured and compared with X-ray filter standards (Pradzynski, 1976) to obtain the element weights: Cr, Mn, Fe, Co, Ni, Cu, Zn and Sr ( $K_{\alpha}$  lines), and Pb ( $L_{\alpha}$  line). Self absorption corrections were made where necessary. The experiment was repeated for pH = 2 and 3. Figure 1 shows the results for pH = 2. It is evident that the element recovery reaches a steady level (not always the maximum level) after 6 or 7 filtrations. Figure 2 shows element recovery after 7 filtrations as a function of pH. It is seen that the best results, taking all 9 monitored elements into account, occur at pH = 2.

Assuming that the portable XRF analyzer has detection limits in the range 4 to 70  $\mu\text{g}$  per  $10\text{ cm}^2$  filter (Rhodes, 1980), we can see that the sample volume must be greater than 50 ml if 1 mg/l element concentrations are to be measured. The capacity of the SA-2 filters was, therefore, tested by monitoring aliquots of the multielement solution having volumes up to 250 ml. Figure 3 shows the X-ray signals for elements Fe, Pb, Zn and Sr as functions of sample volume for constant flow rate (100 ml/min.), number of recirculations (7) and pH (2). The relations are linear.

#### Measurements with Portable X-Ray Analyzer

The feasibility of the SA-2 based preconcentration method was tested by measuring an artificial water sample using the Portable Survey Meter. A water sample was prepared with six elements as pollutants, Ca at 65.5 mg/l, Cr at 4 mg/l, Mn at 4.9 mg/l, Fe at 5.0 mg/l, Cu at 3.7 mg/l and Zn at 4.0 mg/l.



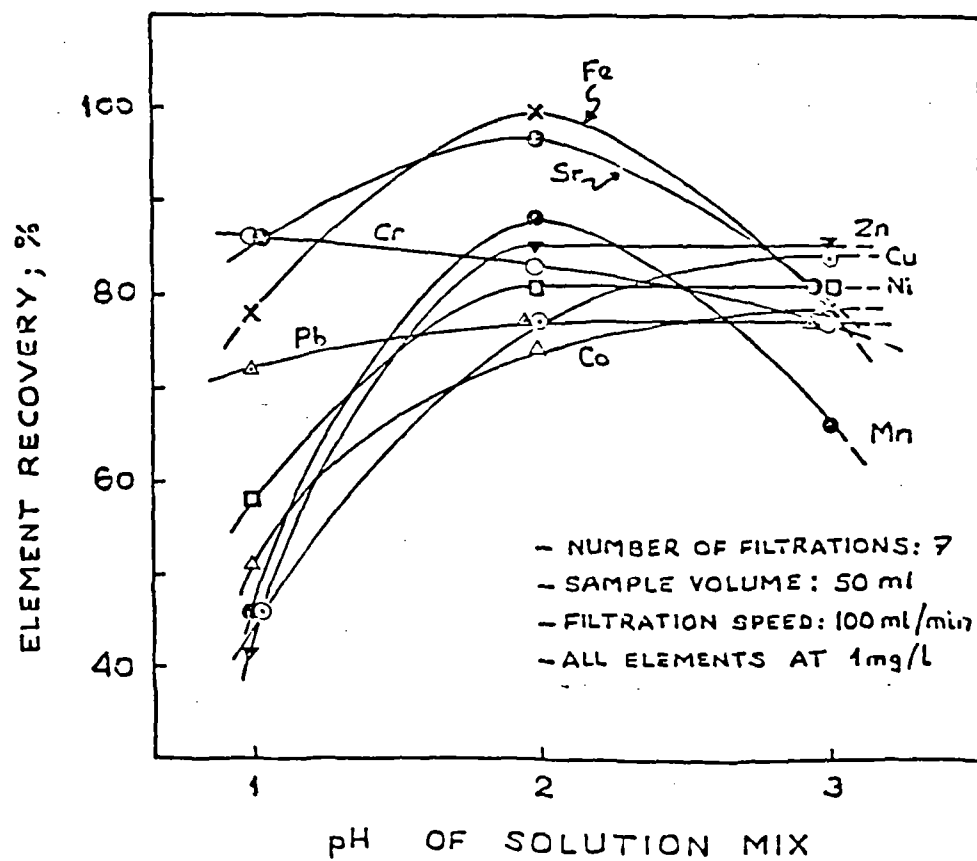


FIG.2 ELEMENT RECOVERY AT VARYING pH

The instrument was calibrated for these elements (except Ca) using thin, single element dried solution standards (Pradzynski, 1976). The standards were measured for 100 sec. with a Cm-244 source. The calibration curves obtained are shown in Figure 4.

Detection limits were determined as 2 standard deviations of the background measured on a blank SA-2 sample. The data are shown in Table 1 for both measurement arrangements, i.e. with and without X-ray filters for energy discrimination (Rhodes, 1980). They are compared with ranges of threshold values for water effluents which can be expected in practice. Detection limits for uranium were measured in a separate experiment using Cd-109 to excite UL X-rays. The detection limits were calculated assuming a sample volume of 250 ml, although the actual sample volume used was 100 ml. The sample was circulated at pH = 2 seven times through the SA-2 disc. The total time of sample preparation was 15 min. including sample drying. The concentrations of elements measured in the sample using the portable instrument are compared in Table 2 with the expected concentrations.

#### DISCUSSION OF RESULTS

The results presented are preliminary. We are aware of some important factors which have to be investigated before the method can be applied for routine use. There are still some doubts as to whether pH = 2 is an optimum value. Some elements are not exchanged at this acidity, for example As and Se. Some important elements have not yet been tested.

The real sample should be filtered through normal filter paper in order to remove any suspended solids prior to its exchange on the SA-2 disc. Possible fractionation of elements between suspension and solution should then be investigated.

The effect of Ca, Mg and Na has to be studied thoroughly. However, we have found that Ca contents up to 65 mg/l have no influence on the recovery of transition elements present in solution.

Uniformity of the sample on the SA-2 paper is an important factor influencing both precision and accuracy. We feel that glass frit is not the proper support for the filters as the frit porosity is not uniform.

TABLE 1. PRELIMINARY SENSITIVITY DATA FOR PORTABLE XRF ANALYZER

Ion Determined	Range of Effluent Limitations <sup>a)</sup> mg/l	Detection Limit; mg/l <sup>b)</sup>	
		With Filters	W/o Filters
Cr <sup>+3</sup>	0.2 to 4.0	0.4	0.2
Mn <sup>+2</sup>	2.0 to 4.0	0.2	0.1
Fe <sup>+3</sup>	0.5 to 7.0	0.2	0.09
Cu <sup>+2</sup>	0.15 to 5.0	0.1	0.07
Zn <sup>+2</sup>	0.5 to 5.0	0.08	0.04
UO <sub>2</sub> <sup>+2</sup>	2.0 to 4.0	0.2 <sup>c)</sup>	0.05 <sup>c)</sup>

<sup>a)</sup> Code of Fed. Reg. No. 40; parts 400 to end.

<sup>b)</sup> Conditions of measurement; 10mCi Cm-244 source and 100 second count per element.

<sup>c)</sup> <sup>3</sup>mCi Cd-109 source used instead of Cm-244.

In spite of the preliminary nature of this work, it does demonstrate the feasibility of rapid field monitoring of waste waters for trace elements using a portable XRF analyzer. The portable analyzer has been developed but the portable preconcentration package has yet to be designed and engineered.

#### ACKNOWLEDGEMENTS

The advice and assistance of J. S. Schindler during the experimental work is gratefully acknowledged. One of the authors (SP) performed the work under the auspices of an International Atomic Energy Agency fellowship.

#### REFERENCES

- Bergmann, J. G.; Ehrhardt, C. H.; Granatelli, L.; Janik, J. L. - "Determination of Sub-ppm Nickel and Vanadium in Petroleum by Ion Exchange Concentration and X-Ray Fluorescence", *Analytical Chemistry*, Vol. 39, No. 11, Sept., 1967, pp 1258 - 1261.
- Bergmann, J. G.; Ehrhardt, C. H.; Granatelli, L.; Janik, J. L. - "Determination of Trace Metals in Terephthalic Acid by Ion Exchange Concentration and X-Ray Fluorescence", *Analytical Chemistry*, Vol. 39, No. 11, Sept., 1967, pp 1331 - 1333.
- Biechler, D. G. - "Determination of Trace Copper, Lead, Zinc, Cadmium, Nickel and Iron in Industrial Waste Waters by Atomic Absorption Spectrometry after Ion Exchange Concentration on Dowex A-1", *Analytical Chemistry*, Vol. 37, No. 8, July, 1965, pp 1054 - 1055.
- Campbell, W. J.; Spano, E. F.; Green, T. E. - "Micro and Trace Analysis by a Combination of Ion Exchange Resin-Loaded Papers and X-Ray Spectrography", *Analytical Chemistry*, Vol. 38, No. 8, July, 1966, pp 987 - 996.
- Campbell, W. J. and Law, S. L. - "Ion Exchange Papers in X-Ray Spectroscopy", *American Lab.*, June, 1970, pp 28 - 34.
- Law, S. L. and Campbell, W. J. - "Resin-Loaded Papers - A Versatile Medium for Sampling and Standardization", *Adv. in XRA*, Vol. 17 (1973), pp 279 - 292.
- Pradzynski, A. H. and Rhodes, J. R. - "Development of Synthetic Standard Samples for Trace Analysis of Air Particulates", *ASTM Special Technical Publication 598*, 1976, pp 320 - 336.
- Rhodes, J. R.; Pradzynski, A. H.; Hunter, C. B.; Payne, J. S.; Lindgren, J. S. - "Energy Dispersive X-Ray Fluorescence Analysis of Air Particulates in Texas", *Environ. Sci. and Tech.*, Vol. 6, No. 10, October, 1972.



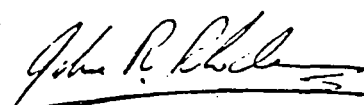
ARD Internal Report 362

APPLICATION OF THE CSI MODEL 740

TO TRACE ELEMENT ANALYSIS OF  
AIR PARTICULATES AND WASTEWATERS

March 1981

Prepared by:

A handwritten signature in dark ink, appearing to read "John R. Rhodes", with a horizontal line drawn underneath it.

John R. Rhodes  
Manager, Applied Research Division  
Columbia Scientific Industries

## 1. INTRODUCTION

The Model 740 is a hand portable low-cost multielement XRF spectrometer suitable for rapid trace element analysis of particulates on membrane filters in laboratory, field or plant conditions. In particular the following determinations are possible by non-scientists on a routine basis:

- 1) Analysis of ambient air particulates after sampling with Hi-vol, dichotomous or other collectors;
- 2) Monitoring of particulate air contaminants in workplace atmospheres after collecting with personal or other samplers;
- 3) Trace metal analysis of industrial wastewaters after preconcentration on, for example, ion exchange resin-loaded filter paper.

There is a rapidly increasing need to monitor air particulates and wastewaters for specific trace elements. Many potentially toxic elements are under intensive study by the Environmental Protection Agency, the National Institute for Occupational Safety and Health and the Department of Energy.

These elements include but are not limited to:

Vanadium	Zinc
Chromium	Arsenic
Manganese	Selenium
Iron	Molybdenum
Cobalt	Cadmium
Nickel	Lead
Copper	Uranium

All these and more can be measured down to microgram levels by the Model 740 Portable XRF Analyzer.

## 2. AIR PARTICULATE SAMPLING

"Ambient" air is usually sampled by "Hi-Vol" samplers (see Figure 1) which draw air through an 8" x 10" filter at about 50 cubic feet per minute for 24 hours. Alternatively, dichotomous samplers are used to produce two air particulate samples, simultaneously, one with a particle size range about .1 to 3 microns and the second with a size range about 3 to 20 microns. The smaller size range is respirable (i.e., lodges in the lungs) while the larger size range has other possible health effects. The elemental composition of the two size ranges is usually markedly different and yields much information about the characteristics of an aerosol, including whether a particular component is man-made pollution or natural dust.

The conventional analysis method is to extract the elements from the filter into water or acid solution. Wet chemistry or atomic absorption is then used for elemental analysis. The process is tedious, time consuming, destructive of the sample and "single-element-sequential" in character. It has been shown that for 20-element analysis, XRF is 6 to 25 times faster than extraction followed by AA. <sup>1)</sup> When the sample is destroyed, it is no longer available for reanalysis in case of disputes, which are common in pollution monitoring.

The only sample preparation needed prior to analysis with the Model 740 is to cut a 1-inch diameter disc from the particulate-loaded filter, place it in the 740 probe (as shown in Figure 2) and press the button to start the measurement. A single 4-minute data accumulation can provide concentration readout for up to 20 elements.

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<sup>1)</sup> Air Quality Instrumentation, Vol. 2, p. 14, Ed. J. W. Scales, Instrument Soc. of America, 1974.

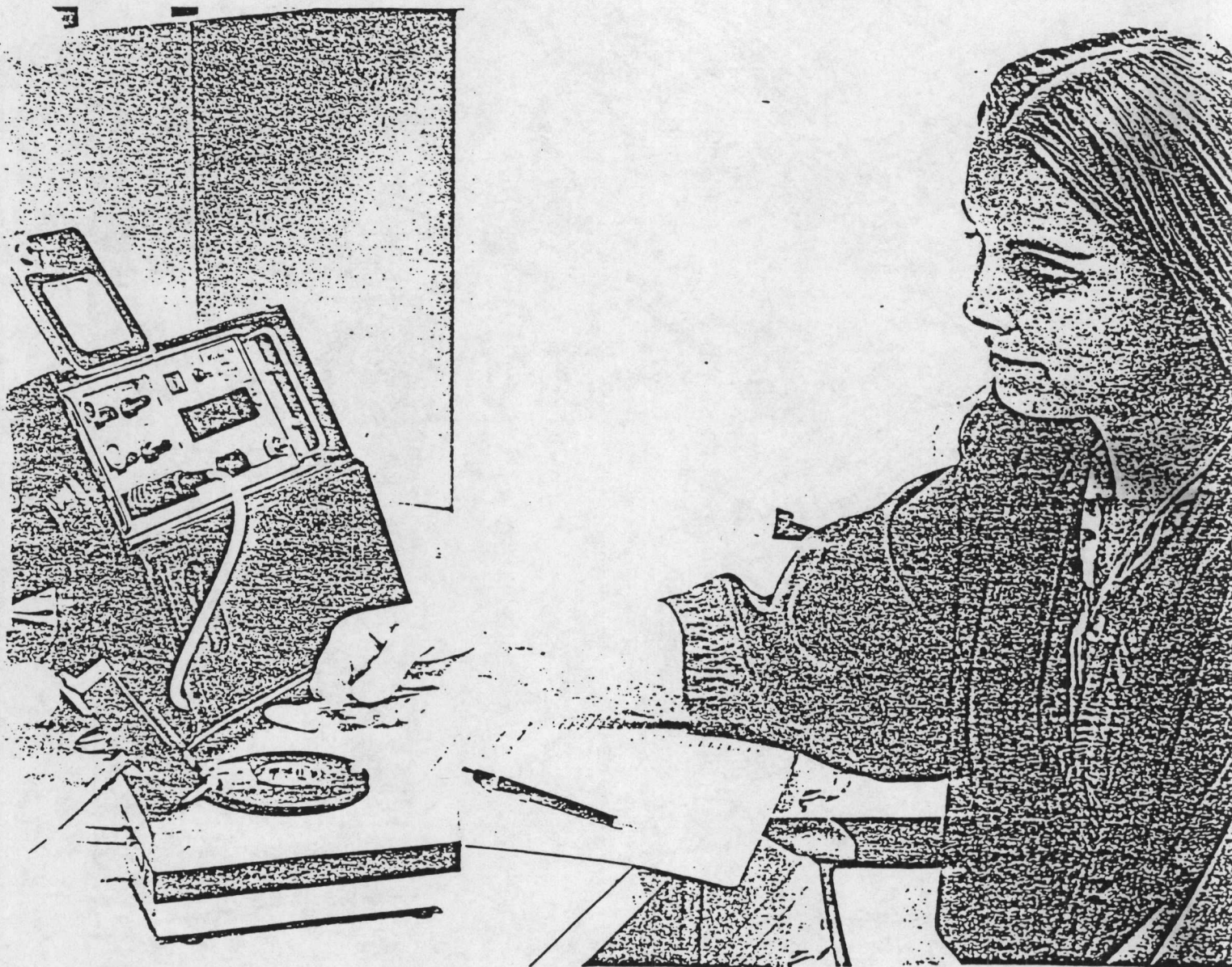


FIGURE 2. PLACEMENT OF LOADED FILTER FOR ANALYSIS





FIGURE 3. PERSONAL DUST SAMPLER



## 5. SENSITIVITY

Table 1 lists values of interference-free detection limit for all elements normally determined by the Model 740 using standard excitation conditions. Although they refer to air particulates on membrane filters, the values shown can also be used as a guide to sensitivities obtainable with other substrates such as ion exchange resin-loaded filters and cellulose or quartz fiber air filters.

In a single count all the elements detected by a given probe can be measured and their concentrations read out in groups of 4 at a time. The concentrations can be read out by the instrument in any desired units ( $\mu\text{g}/\text{cm}^2$ ,  $\mu\text{g}/\text{M}^3$ ,  $\text{mg}/\text{M}^3$ ,  $\mu\text{g}/\text{l}$ ,  $\text{mg}/\text{l}$ , etc.) if so calibrated beforehand. Table 2 shows how the basic detection limit in  $\mu\text{g}$  element per  $\text{cm}^2$  of filter can be converted to "practical" units by including the sampling or preconcentration information.

Comparing Tables 1 and 2 shows that, since the basic detection limit for most of the elements is below  $0.5 \mu\text{g}/\text{cm}^2$ , the sensitivity of the method is entirely adequate for almost all industrial air contaminant and wastewater analyses and many ambient air particulate analyses. Table 3 lists some elements that are potential air contaminants in the workplace together with their Threshold Limit Values and corresponding detection limits using the C.S.I. Model 740 in a 4-minute analysis of an 8-hour personal air filter sample. Another example is shown in Table 4 which lists some typical heavy metal contaminants in industrial wastewaters together with their maximum permissible concentrations in effluent and their detection limits using the Model 740. This is an impressive demonstration of the sensitivity obtainable by this rapid, non-destructive, low-cost technique.

TABLE 1 - CONTINUED

<u>Element</u>	<u>Detection Limit (<math>\mu\text{g}/\text{cm}^2</math>)</u> <sup>1)</sup>	<u>Probe</u>	<u>Source</u>
Nb	0.41	Standard	3 mCi Cd-109
Mo	0.46	"	"
Ru	4.6	Heavy Element	10 mCi Am-241
Rh	4.0	"	"
Pd	3.6	"	"
Ag	3.5	"	"
Cd	3.7	"	"
In	4.4	"	"
Sn	5.4	"	"
Sb	6.2	"	"
Te	7.0	"	"
I	7.6	"	"
Cs	8.1	"	"
Ba	8.1	"	"
Ta	0.7	Standard	3 mCi Cd-109
W	0.6	"	"
Hg	0.5	"	"
Pb	0.4	"	"
U	0.7	"	"

1) 2 standard deviations of the blank in one 4-minute count

Note: Increased sensitivity can often be obtained for specific groups of elements.

TABLE 3

EXAMPLES OF SENSITIVITY FOR SOME WORKPLACE AIR CONTAMINANTS

Element	Source	TLV <sup>a)</sup> ( $\mu\text{g}/\text{M}^3$ )	Detection Limit ( $\mu\text{g}/\text{M}^3$ ) <sup>b)</sup>
P	Fe-55	100 to 300	12
Ca	Fe-55	10000 to 20000	0.9
V	Fe-55	50 to 1500	1.2
Cr	Cd-109	500	6.5
Mn	Cd-109	5000	5.7
Fe	Cd-109	1000 to 10000	5.2
Ni	Cd-109	100 to 1000	4.2
Cu	Cd-109	200	3.8
Zn	Cd-109	1000 to 20000	3.5
As	Cd-109	500	2.9
Pb	Cd-109	150 to 450	4.1
U	Cd-109	200 to 600	7.4
Zr	Cd-109	5000	3.8
Mo	Cd-109	5000 to 20000	4.6
Cd	Am-241	50 to 150	37
Sn	Am-241	2000	54
Sb	Am-241	500	61
Ba	Am-241	500	81

a) Threshold Limit Value - lower value quoted is 8-hour Time Weighted Average, upper value is Short Term Exposure Limit. (ACGIH, 1977)

b) Based on 8-hour Sample at 2 l.p.m. flow rate through 37mm dia. membrane filter.

# THE APPLICATION OF X-RAY FLUORESCENCE TECHNOLOGY IN THE CREATION OF SITE COMPARISON SAMPLES AND IN THE DESIGN OF HAZARDOUS WASTE TREATABILITY STUDIES

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## ABSTRACT

Site Comparison Samples (SCS) and treatability studies are contemporary tools used in the investigation and remediation of hazardous waste sites. Each depends on the development of large volume samples which are characteristic of the most difficult conditions at a site to treat. The use of X-ray fluorescence spectrometers (XRF) to identify sample locations at a major Superfund site is described. The subsequent processing of samples into SCS materials and treatment samples is presented.

## INTRODUCTION

As byproducts of a growing technological society continue to find their way into the environment, the Environmental Protection Agency (EPA) must face an ever-expanding problem of how to handle and measure the harmful byproducts. Before contaminants can be removed or neutralized, they must be characterized for type and quantity. Field-Portable X-ray Fluorescence (FPXRF) instrumentation has been shown to be useful as a screening tool for heavy metals in soils at hazardous waste sites (1,2). Instruments are smaller than their laboratory counterparts, transportable by a single individual, hermetically sealed, and provide immediate data from analyses completed with little or no sample preparation. Analyses are either conducted in a field laboratory or in situ.

The Bunker Hill Superfund Site is located in the Coeur d'Alene mining district of northern Idaho. The site is 7 miles by 3 miles. Primary site contaminants are lead and zinc associated with the mining, beneficiation, smelting and refining of lead-zinc-silver ores. Lead smelting commenced in 1917 and zinc refining operations began in 1927. Operations ceased in 1981. Over the period of operation of these facilities, metals were emitted to the atmosphere from both point and fugitive sources. Tailings from the beneficiation operations were discharged to the Coeur d'Alene River prior to the construction and use of tailings impoundments. These emissions and discharges resulted in widespread contamination of area with metals (3).

The management of large, complex Superfund sites requires years of effort by many parties, and is composed of a series of individual projects and concurrent tasks. Each task requires development of its own quality assurance plan. Quality control within and between projects relating to the same site is an

important element of an overall quality assurance program. Due to the size of the site (21 square miles), the number of parties involved, and the length of time until remediation is complete, the use of Site Comparison Samples (SCS) as tools for applied quality control allow quality assurance of data between projects on the same site.

As a result, two requirements presented themselves simultaneously:

- (1) The need to develop large, homogenous volumes of heavily contaminated soils for treatability studies, and
- (2) The need to develop large homogenous samples of soils which should be processed as Site Comparison Samples ("SCS project").

Field screening using FPXRF technology was selected as the analytical tool to ensure that appropriate soils were developed for both of these purposes.

## FIELD ACTIVITIES

Over 500 kilograms of soil was required for the site studies and the SCS project. The soils needed to be heavily contaminated and as dry as possible. Authorization to proceed was received in October 1987. Then current weather conditions in northern Idaho were unusually dry for that time of year; hence, any field effort had to be mobilized quickly or postponed until the following summer. Postponement was not acceptable. The high cost of the treatability studies and the critical nature of the SCS project to the long term quality control program at the site demanded that soils of known concentrations with known data quality be obtained; sample collection without concurrent analysis was not acceptable. Field activities needed to be supported, therefore, with instrumentation that could be mobilized quickly, be portable enough to be moved throughout a large site and be capable of providing analytical responses to field personnel on a "real-time" basis.

## Equipment

The FPXRF used at Bunker Hill is the X-Met 840 manufactured by Columbia Scientific Industries Corporation. A technical description highlighting its applicability for use at hazardous waste sites is provided by Piorek and Rhodes (4). The X-Met 840 is a

self-contained, battery powered, microprocessor-based, multichannel X-ray fluorescence analyzer weighing 8.5 kg. The surface analysis probe is specially designed for field use. The X-Met 840 is hermetically sealed and can be decontaminated with soap and water. The probe includes a radioisotope source of Curium-244, a proportional counter and the associated electronics. The source is protected by an NRC-approved safety shutter.

The electronic unit has eight calibration memories called "models". Each model can be independently calibrated for as many as six elements each. These can be used to measure elements from aluminum up to uranium assuming two probes with the associated isotope sources are available. The unknown sample intensities are regressed against the calibration curves to yield concentrations. For the Bunker Hill site only lead and zinc were investigated and only two models were calibrated. Model 1 was calibrated from background up to 4980 mg/kg Pb and 9791 mg/kg Zn.

#### Reference Soil Standards for Quality Control and Standardization

The commercially available FPXRF systems use standards to establish calibration curves for comparison. Heretofore there has not been a demand for FPXRF systems in hazardous waste screening. Because of this low demand, there were no standards commercially available until recently. Columbia Scientific Industries Inc. (CSI) has produced the first set of commercially available standards designed specifically for hazardous wastes in soils. The primary calibration curves are based on these standards, which are listed in Table I as CSI. A description of a calibration technique for X-Ray Analyzers used in hazardous waste site screening is presented by Piorek and Rhodes (5).

#### Sampling

Sampling was completed in two days. Formerly acquired metals data was reviewed to identify several potential areas for field screening. These were visited in an attempt to limit the number of areas actually screened with the FPXRF. Three areas ranging in size from less than one to greater than 10 acres appeared to be appropriate, i.e., existing data suggested heavy contamination at those locations, the soil matrix was typical of the area, the areas were accessible and dry, and samples processing could be accomplished without disrupting other activities.

FPXRF screening was accomplished in two steps. First, a series of stations were staked and located on site maps. A two-person crew was used, one to set stakes and one to map the sample locations using a Brunton compass and a 300 foot tape. Second, a two-person FPXRF crew completed on site screening at each station. One person operated the instrument and one served as data recorder.

FPXRF data was acquired at each of the three target areas at a rate which exceeded one data point per two minutes. The rate limiting factor at each target area was the time required to survey the sampling grid, not to operate the FPXRF instrument. It might have been possible to eliminate the second person on the FPXRF crew without compromising the data acquisition rate. More time was required to move between target areas than to sample once the team was in an area. Typical

FPXRF measurement times were 20 seconds per data point.

The levels of contamination as measured by the FPXRF for stations within the three areas ranged from 2300 to 70,000 mg/kg for lead, and 750 to 27,000 mg/kg for zinc. These values cannot be compared directly to contaminant values as obtained by standard SW 846 methods or CLP methods because they use partial digestions or extracts for analysis and FPXRF provides total elemental (or bulk) analyses.

Based on a review of these data, bulk soils were collected at two target areas between stations exhibiting the highest contamination levels. Sixteen samples, each with a field weight of at least 60 pounds was collected. Prior to shipping, each of these was analyzed in duplicate for lead and zinc by the FPXRF. Lead contamination in the samples ranged from 15,000 to 67,000 mg/kg. Zinc ranged from 1900 to 28,000 mg/kg. Samples with this level of contamination were adequate for both the SCS project and the treatability studies.

#### SCS DEVELOPMENT

As analytical instrumentation has moved into the field to complement laboratory instrumentation, so have the inherent problems of quality assurance and the application of field quality control to compare to data produced by established "conventional" methods of sample analysis. Given the problems of variability in results caused by selection of sampling points on a site, or by variability in relative large volume samples later analyzed by small aliquot "high sensitivity" methodologies, project officers and sample plan designers have turned to two recognized QC procedures to establish comparability; splitting samples between analytical facilities and increased use of Standard Reference Materials. With the increased use of contract laboratory facilities, the problems have increased disproportionately with each added analytical facility introduced in the larger multiple party sites. Cost and resource expenditure in time and logistics increase.

#### Definition

"A Site Comparison Sample (SCS) is a site specific reference material which is representative of the type of problems encountered when analyzing or treating materials from the site." SCS's:

- Contain key contaminants in the matrix of the site;
- Are available in sufficient numbers to satisfy numerous site management and QA/QC purposes;
- Exhibit the lowest possible coefficient of variation (cv);
- Are managed by an organization capable of being a depository of analytical results, providing a common management point for quality assurance, inter- and intra-laboratory studies.

SCS differ from Standard Reference Materials (SRM) by virtue of being site specific, and not produced under a protocol requiring the pre-release rigorous analytical method specific, statistically validated



characterization applied to SRMs. They also differ from Performance Evaluation (PE) samples used in studies to directly compare inter-laboratory results under a defined methodology. A SCS stock could conceivably provide the material for a SRM or PE, but would require those protocols to be applied before so identifying.

Quality assurance of data developed from multiple sources presents a complex situation. One major problem is the question of sample variability and comparability caused by distribution of compounds of interest on a site. A second is the variability inherent in, and between, analytical methods, particularly due to matrix interference effects. Two common techniques for dealing with these problems are the use of "split" samples and analyses of Standard Reference Materials. Splitting increases the risk of magnifying the problem due to distribution; standard reference materials seldom reflect the matrix effects present in "natural" site samples.

Late in 1984 and early in 1985, the concept of manufacturing a homogenized bulk sample was developed to provide vendors of proprietary soil stabilization services uniform materials for evaluation. The use of screening techniques to define areas of concern on a site was directly applied to statistically choosing sources of material to provide a sample representative of the more highly contaminated material distributed in the matrix of the site. Mixing methods were investigated from the viewpoints of cost, available resources, and practicality. Separate elements of the methodology were tested on available materials at various sites. Protocols and standard operating procedures regarding from where to select the material, how to homogenize it, and how to fill the bulk sample containers in a manner that would reduce bias in the distribution of the material to the large bulk containers were developed.

The question of how to mix bulk samples of site matrix materials to achieve a relatively homogenized material had to be answered empirically. Because of the wide variety of particle sizes, moisture content, cohesive characteristics and distribution of contaminants, it was decided to thoroughly mix the material for the first 1400 pound sample by manually quarter piling through several cycles; and then do a multiple random fill of enough buckets (sixty-nine) to meet all projected needs. It was labor intensive, and took 4 people most of one day.

The sequence of events discussed in the creation of the bulk reference materials led logically to the concept of further treatment of the bulk material to provide a "Site Comparison Sample (SCS)" for each major site. Initially, approximately two dozen 8 oz. sample containers were "broken out" of a bucket, and used for comparative analyses to determine the degree of mixing achieved. Some pressure was felt to supply some of these for comparison analyses instead of splitting samples. At that time, resources were not available to so use the material; no statistically sound evaluation of the material existed to back up any results.

It cannot be emphasized too heavily that the SCS is not be considered a sample that represents the actual concentration of a contaminant at any given point on a site. Also, it cannot initially be considered as a true SRM, although it may be possible to up-grade it's status if a large number of SCS are generated, and enough

analytical resources are available to utilize a portion of the banked samples for a statistically sound standardization analyses. The concept of the SCS is to produce a material that can be used in lieu of split samples, and provide a data bank for both continuing and retroactive analysis of variation due to differing methods of sample acquisition, handling, and analyses. As the discrete SCS will be archived in controlled storage, the effects of holding time can be demonstrated for each set by continuing characterization analyses. The more SCS analyzed, the stronger the statistical evaluation of all data generated by analyses becomes; not only of the SCS bank itself, but of the sample of record data and the laboratories producing the data.

In Statistics there is the "The Central Limit Theorem": It states:

"From an unknown distribution a random sample size  $n$  is obtained. If  $n$  is allowed to become larger, the sample mean will behave as if it came from a Normal distribution, regardless of what the parent distribution looked like."

John Webber, Statistician for EPA Office of Policy and Planning, had provided a table illustrating how Normality affects a sample population (Table II) taken from a universe, and reverse logic suggests that very low variances could be expected from discrete samples of  $n_h$ , especially if the discrete samples were produced by actually filling the randomly selected sample containers with a series of multiple portions selected at random from the bulk  $n_h$  material. (The "double random" referred to hereafter.)

Reasoning from this point, if  $n$  is sufficiently large, and then thoroughly mixed or homogenized, multiple random creation of  $n_h$  should result in a low variance that approaches the "true" value of the concentration of the mean of  $n$ . As the number of random selections used to create  $n_h$  increases, the coefficient of variation should decrease.

Through the balance of 1985 and into 1986, the analytical results from the stabilization tests made on the bulk materials were reviewed. Protocols were developed through experimentation to mix sludges of water, sediment and hydrocarbon products. A protocol for groundwater SCSs was developed.

Finally, in late 1986 an opportunity presented itself to produce an actual SCS for a large, established Superfund site. This dovetailed with the trial of the X-Met FPXRF equipment, and made it possible to more soundly screen the bulk "raw material" for both stabilization studies and two SCSs; one "high" range and one "low" range. A fairly ambitious design was proposed to produce between 300 and 500 8 oz. samples in each range.

Experience with the homogenization of the original stability samples suggested that it would be desirable to utilize more efficient methods of mixing the bulk sample material. Accordingly, a "drum roller" was obtained, and 55 gal O.T. steel drums were modified with two interior deflection vanes similar to those used in industrial dry mixing of materials. The bulk sample material was batched through this drum and then spread out in a distribution box for the double random selection of the SCS samples. The available quantity of material dictated that only a single SCS be produced, so the "high" and "low" bulk retains were incorporated into

a single batch for processing.

The 600 aliquots have been "banked", and a master random distribution list prepared. From the bank, an initial set of 10 SCS (the first block on the list) were supplied to the USEPA Environmental Monitoring Services Laboratory, Las Vegas, NV. for preliminary characterization analyses. At the same time, a principle contractor was issued the next 30 samples for release to their contract laboratories for the same purpose. All analytical data results are to be reported to Region 10, and a running control chart of results developed.

As the number of samples analyzed increases, the data will become progressively more refined, and amenable to other statistical analyses to more closely define the sources of variability, from laboratory, to method, and to a certain extent, the effects of holding time. Data currently available are presented in Figures 1 and 2. Although the number of data points are limited, there is a suggestion that inter-laboratory differences may be important (Figure 1), and that overall cv's are low (less than 30%).

As related, this is an ongoing developmental effort. Preliminary data indicate the approach is sound. For middle to large site hazardous waste operations, and for long term ambient monitoring projects, the economies of scale would apply. For improved data quality and scientific credibility the concept is entirely appropriate and defensible. The practical application awaits resources and initiatives on the part of the user programs.

#### REFERENCES

- (1) Chappell, R. W., Davis, A. O., Olsen, R. L., "Portable X-Ray Fluorescence as a Screening Tool for Analysis of Hazardous Materials in Soils and Mine Wastes," the 7th National Conference of Management of Uncontrolled Hazardous Waste Sites, Hazardous Materials Control Research Institute, Silver Spring, Maryland, 1986.
- (2) Raab, G. A., D. Cardenas, and S. J. Simon, "Evaluation of a Prototype Field-Portable X-Ray Fluorescence System for Hazardous Waste Screening," EPA/600/4-87/021, U.S. Environmental Protection Agency, Las Vegas, Nevada, 1987.
- (3) Gulf Resources and Chemical Corporation, "Bunker Hill Site Remedial Investigation/Feasibility Study for Unpopulated Areas," April 24, 1987.
- (4) Piorek, S., Rhodes, J. R., "Hazardous Waste Screening Using a Portable X-ray Analyzer," Symposium on Waste Minimization and Environmental Programs within DOD, American Defense Preparedness Association, Long Beach, California, April 1987.
- (5) Piorek, S., Rhodes, J. R., "A New Calibration Technique for X-Ray Analyzers Used in Hazardous Waste Screening"

Table I  
Concentrations of Standards

Standard Elements:		Pb	Zn	Cu	As
Name					
(All values are in mg/kg)					
1	CSI 1B	0	4790	4790	6970
2	CSI 2B	0	0	0	11,340
3	CSI 3B	4980	0	0	0
4	CSI 5B	240	240	8160	7740
5	CSI 6B	484	482	6300	5590
6	CSI 7B	4760	4900	3810	11,070
7	CSI 8B	1474	983	2950	4530
8	CSI 9B	1990	2970	982	3390
9	CSI 10B	2930	3910	1960	2250
10	CSI 11B	2440	6360	490	1140
11	CSI 12B	3405	8270	243	565
12	CSI 13B	4126	9791	96	224
13	CSI 14B	0	0	4950	0
14	CSI 15B	0	4950	0	0

Table II  
Illustration of How Normality Affects Samples

Let us phrase the question "How many samples do I need to be within Q sigma "s" (Standard Deviations) of the true value?":

Q Sigma "s"	Confidence 90%		Confidence 95%		Confidence 99%	
	Normal	Worst Case	Normal	Worst Case	Normal	Worst Case
2s	1	3	1	5	2	25
1s	3	10	4	20	6	100
0.75s	5	18	7	36	10	178
0.5s	11	40	16	80	22	400
0.4s	17	63	25	125	34	625
0.3s	31	112	43	223	61	1112
0.2s	68	250	97	500	136	2500
0.1s	271	1000	385	2000	543	10000

from: "Statistical Considerations in Sampling Hazardous Waste Sites", John Warren,  
E.P.A./O.P.R.M.

Figure 1  
BETWEEN LABORATORY COMPARISON

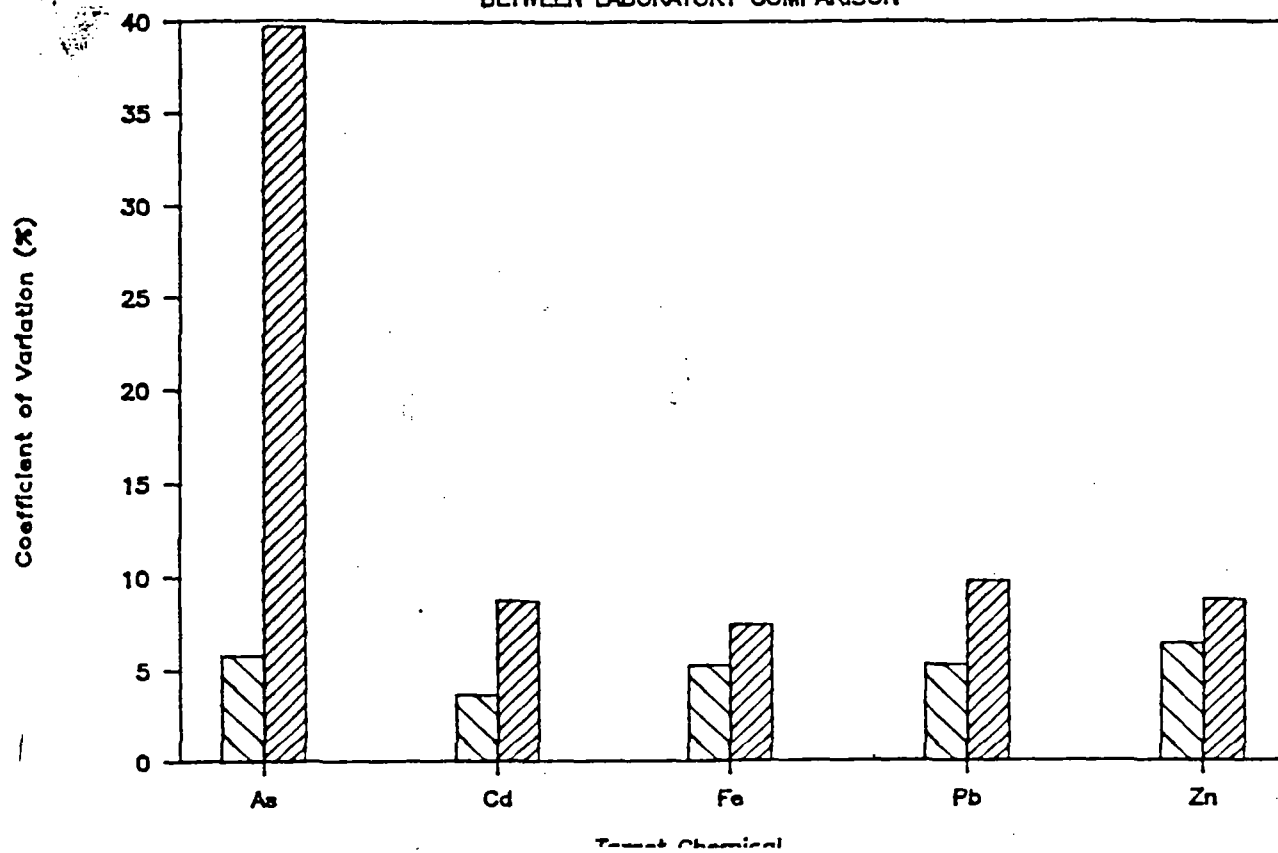
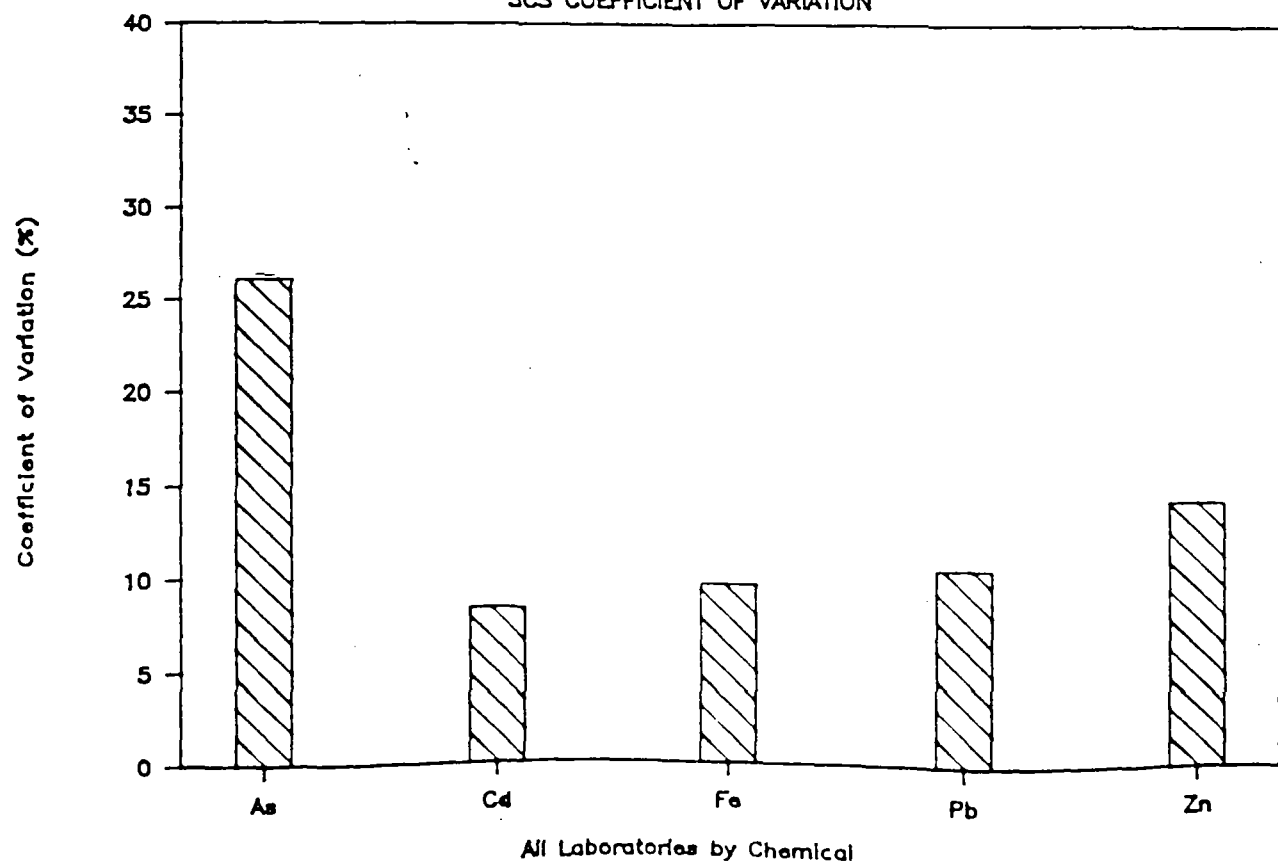


Figure 2  
SCS COEFFICIENT OF VARIATION



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Camp Dresser & McKee, Inc. 2300 15th Street Suite 400 Denver, CO 80202	Rick Chappel 303-458-1311	HEPS-Cm HEPS-Am (840)	Hazardous Waste (Mine tailings)
Dept. of Defense 1450 Queen Avenue S.W. Albany, OR 97321	Dr. Bill Reily 503-967-5851	SAPS-Cd (840)	Scrap Sort. & Waste
Ecology & Environment 6440 Hillcroft Houston, TX 77081	Jack McLaughlin 713-771-9460	HEPS-Cm (880)	Hazardous Waste
Ecology & Environment 101 Yesler Way Seattle, WA 98104	Mike Bray 206-624-9537	DOPS Cd/Am (880)	Hazardous Waste
Etna Products 16824 Park Circle Drive P. O. Box 630 Oils Chagrin Falls, OH 44022	Mike Bell Rod Schaffter 216-543-9845	HEPS-Fe (820)	Chlorine in oil
Envirosafe Services 1602 W. Franklin P. O. Box 417 Boise, ID 83701	Barry Buckendorf 208-834-2275	HEPS-Cm HEPS-Am LEPS-Fe (840)	Hazardous Waste (dump site)
Hittman-Ebasco Services, Inc. 9151 Rumsey Columbia, MD 21045	Craig Rice 301-730-8525	HEPS-Cm (840)	Hazardous Waste
State of Indiana 105 S. Meridian Street P. O. Box 6015 Indianapolis, IN 46206-6015	Greg Busch 317-232-8933	HEPS-Cm HEPS-Am (840)	Hazardous Waste
Lockheed EMSCO 1050 E. Flamingo, #120 Las Vegas, NV 89119	Greg Raab 702-734-3332	DOPS Am/Cm (880)	Hazardous Waste (Technology transfer)
Martin Marietta P. O. Box 2002 Oakridge, TN 37831	Frank Dyer 615-574-4871	HEPS-Cm SAPS-Cm (840)	Hazardous Waste
P.T.I. Env. Services 317 S.W. Alder, Suite 1135 Portland, OR 97204	Charles Lytle Gary Bigham 206-643-9803	SAPS-Cm (840)	Hazardous Waste

(Level  
II)

WORK



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Stan Daigle  
Bob Koester  
713-692-9151

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(840)

Alloys  
Pb-Wall  
Paint

U.S. E.P.A.  
215 Fremont Street  
San Francisco, CA 94105

Matt Monsees  
Bill Lewis  
415-974-7464

SAPS-Cm  
(840)

Hazardous  
Waste

U.S. Pollution Control, Inc.  
Suite 400 S.  
2000 Classen Center  
Oklahoma City, OK 73106

Bruce Bennett  
801-678-3344

DOPS Cm/Am  
(880)

Hazardous  
Waste

Jacobs Engineering  
12600 W. Colfax Ave.  
Suite A300  
Lakewood, CO 80215

Gary Miller  
303-232-7093

SAPS-Cm  
(840)

Hazardous  
Waste  
(Mine  
tailings)

Envirosafe Services  
876 Otter Creek Rd.  
Oregon, OH 43616

Joanie Wilhite  
419-726-1521

(2) HEPS Cm/Am  
(820)

Hazardous  
Waste  
(Dump site)

U.S. Dept. of Energy  
Martin Marietta Systems Div.  
Plant X-10  
Oak Ridge, TN 37831

John Nyquist  
615-574-4646

SAPS-Cm  
(880)

Hazardous  
Waste

Eppert Oil  
9100 Freeland  
Detroit, MI 48228

Claudia Graham  
313-273-7374

HEPS-Fe  
(820)

Hazardous  
Waste  
(Chlorine  
in oil)

NUS Corp.  
3280 River Road  
Cincinnati, OH 45204

Scott Engle  
513-251-2730

SAPS-Cm  
(840)

Hazardous  
Waste  
(Air parti-  
culates on  
filters)

State of New Jersey  
Windsor Industrial Park  
Main Street (18A)  
Windsor, N.J. 08561

James McCarthy

DOPS Cm/Am  
(2) (880)

Hazardous  
Waste

Chen-Northern  
Box 4699  
Helena, MT 59604

Dave Hazen  
406-443-5210

SAPS Cm  
SAPS Am  
(840)

Hazardous  
Waste

N.E.I.C.  
Denver Federal Center  
Bldg. 45, Door S-2  
Denver, CO 80225

Chuck Ramsey  
Don Smith  
303-236-5132

DOPS Cm/Am  
(880)

Hazardous  
Waste